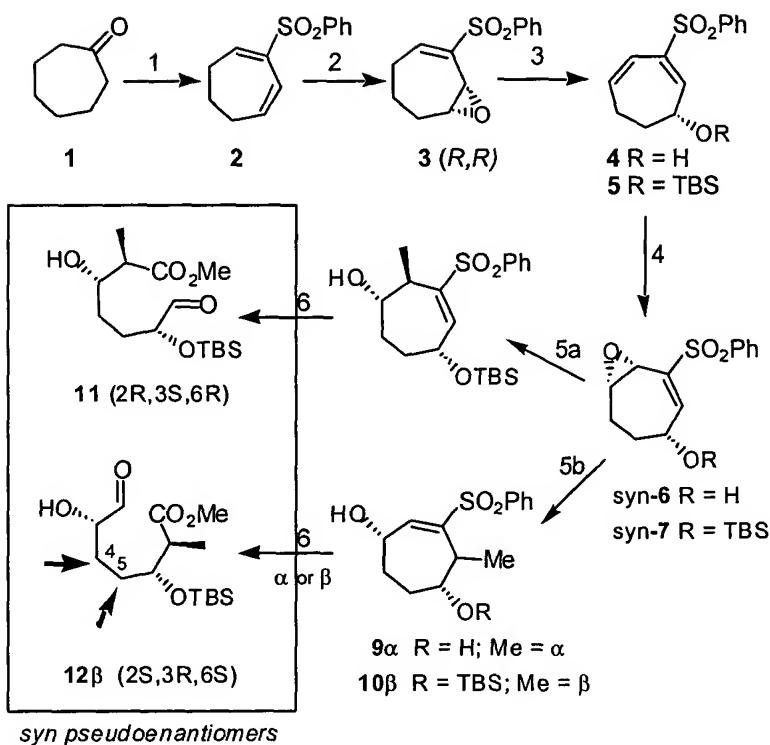


FIGURE 1



Scheme 1. Preparation of acyclic arrays

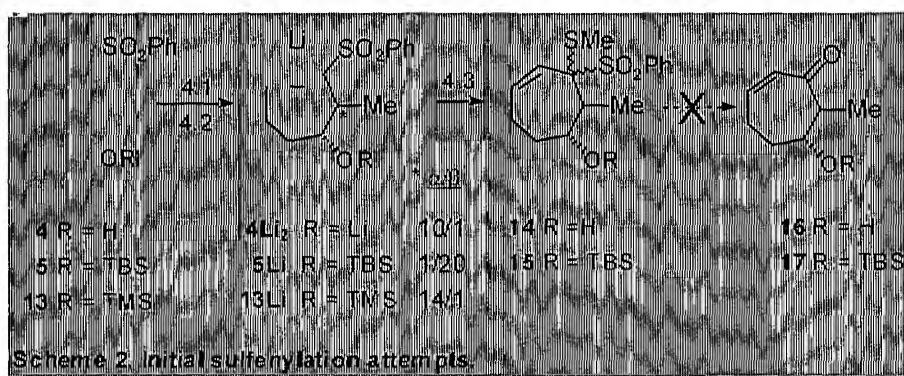
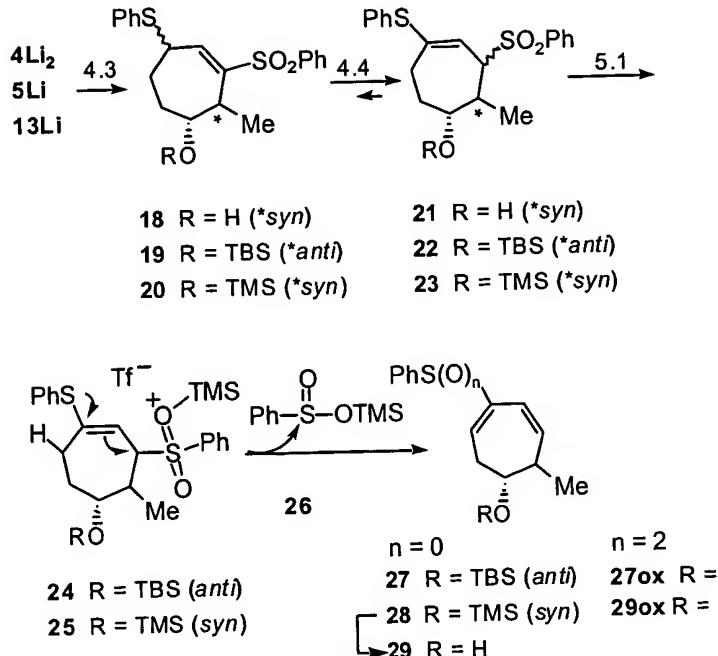
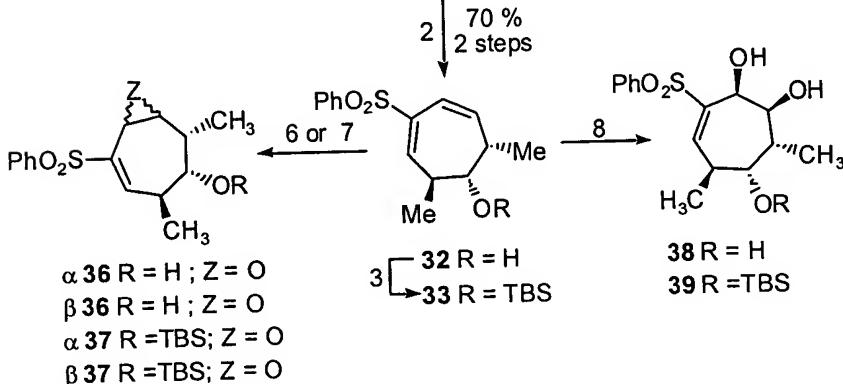
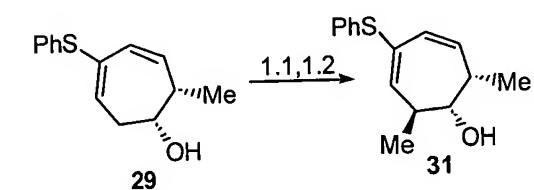
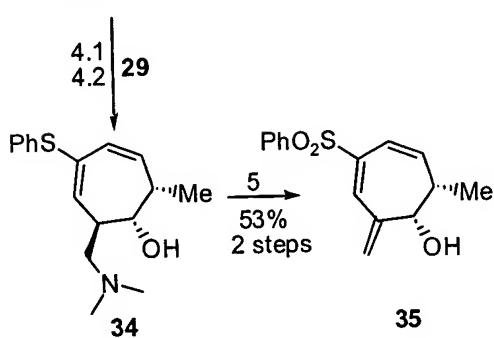
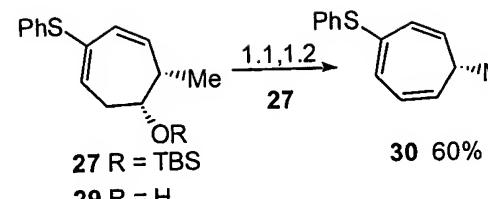


FIGURE 2



Scheme 3. Novel gamma sulfenylation and diene transposition.

FIGURE 3



Scheme 4. Preparation of stereopentad progenitors. 1.1 *n*-BuLi (2.2 eq), THF, -78°C to -7°C, 1.2 MeI (5 eq), -90°C to -50°C; 2 *m*-CPBA (2.2 eq); CH₂Cl₂, 25°C, 30 min; 3 TBSOTf (1.2 eq), Lutidine (2 eq), CH₂Cl₂, 25°C, 2 h; 4.1 *n*-BuLi (2.2 eq), THF, -78°C to -5°C, 90 min; 4.2 Eschenmoser's salt (2.5 eq), THF, -70°C to 0°C, 1.5 h; 5 *m*-CPBA (4 eq); CH₂Cl₂, 25°C, 1 h; 6 TBHP + 5% Mo(CO)₆, 88% >15:1 α/β ; 7 10% (*R,R*)-Mn(salen)Cl, H₂O₂, 1 eq NH₄OAc, 83% 1:>20 α/β , 8 OsO₄ cat. >80%, single diastereomer

FIGURE 4

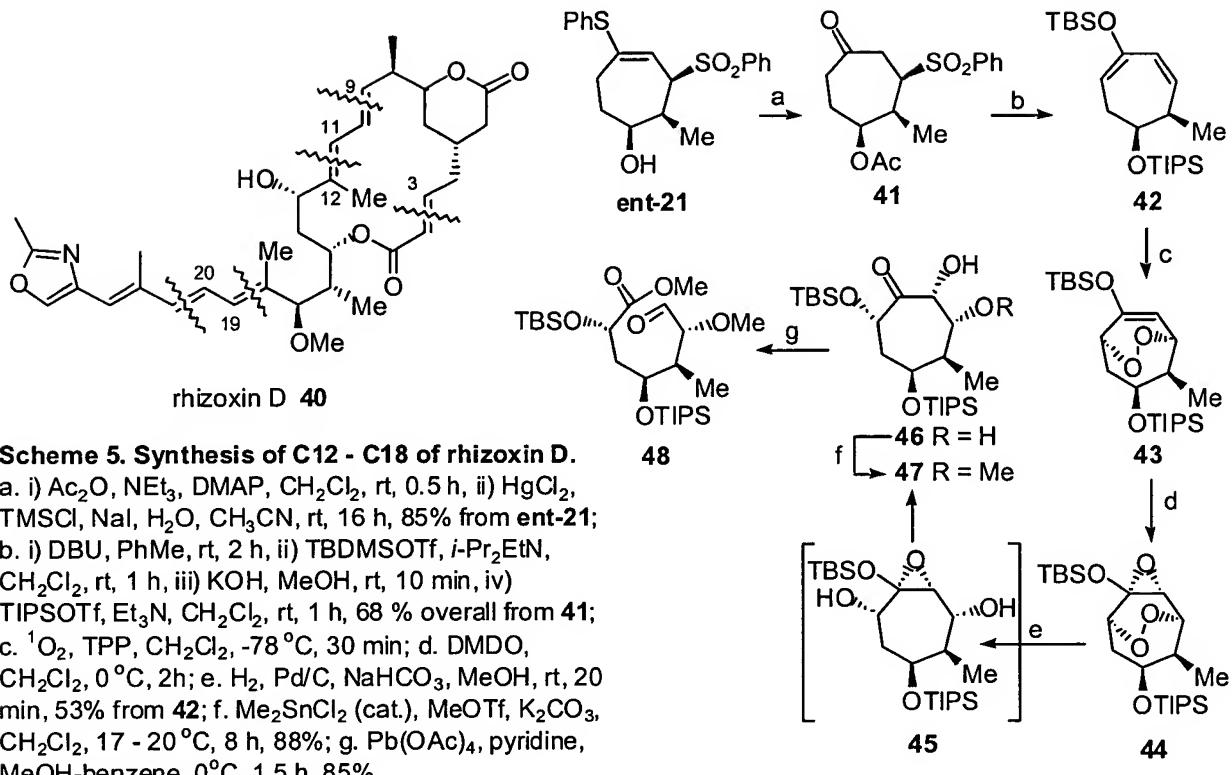
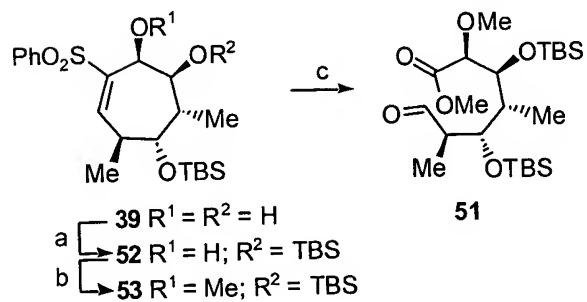
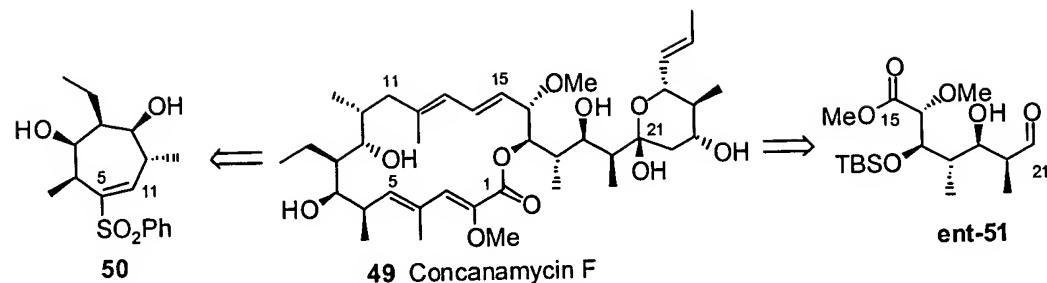
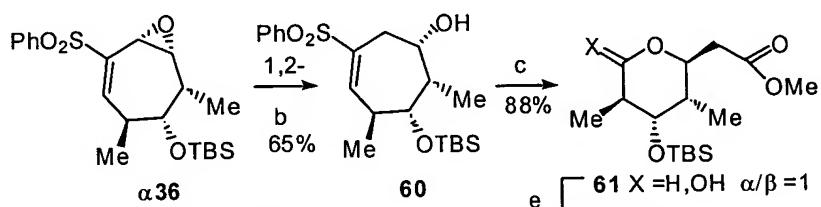
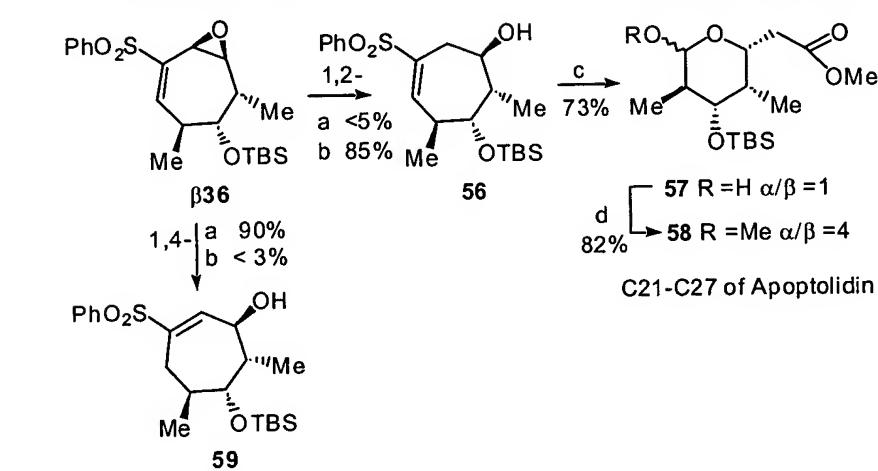
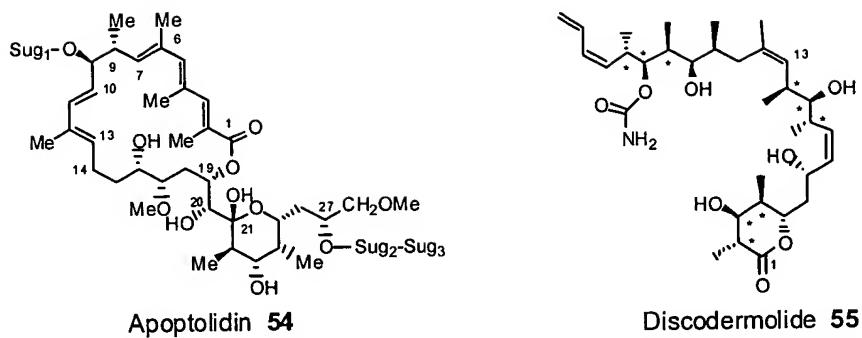


FIGURE 5



Scheme 6. Synthesis of the ent-C15-C21 fragment of Concanamycin F.
 a TBSOTf , 2,6-Lutidine, CH_2Cl_2 , -78°C , 24 h, 99%; b $\text{KOH}/\text{MeI}/\text{DMSO}$, 25°C , 5 min; 94%; c O_3 , CH_2Cl_2 , MeOH (1:2), NaHCO_3 , -78°C , 5 min, then PPh_3 , 92%

FIGURE 6



Scheme 7. Preparation of C21-C27 of

Apoptolidin and C1-C7 of Discodermolide.

a $\text{BH}_3 \cdot \text{THF}$ (1.6 eq), THF, 0°C, warm to 25°C, 12 h;

b 1.5 eq DIBAL-H, -78°C; c O_3 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$

(1:2), NaHCO_3 , -78°C, 5 min; d Ag_2O , MeI , CH_3CN , reflux, 3 h; e PDC (5 eq), CH_2Cl_2 , 25°C, 10 h

FIGURE 7

FIGURE 7
Figure 1. Evaluation and importance of the sulfur atom for this synthesis.

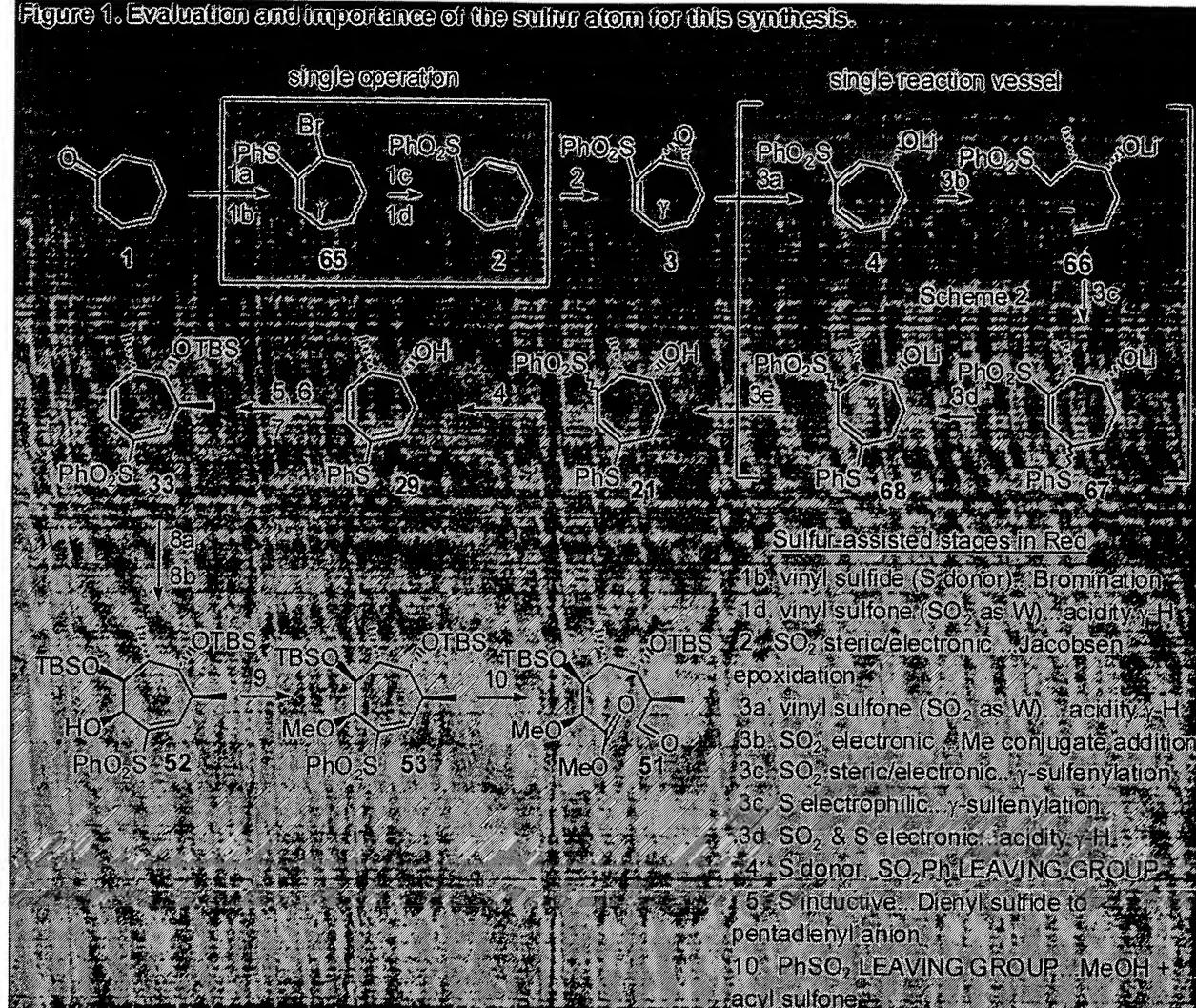
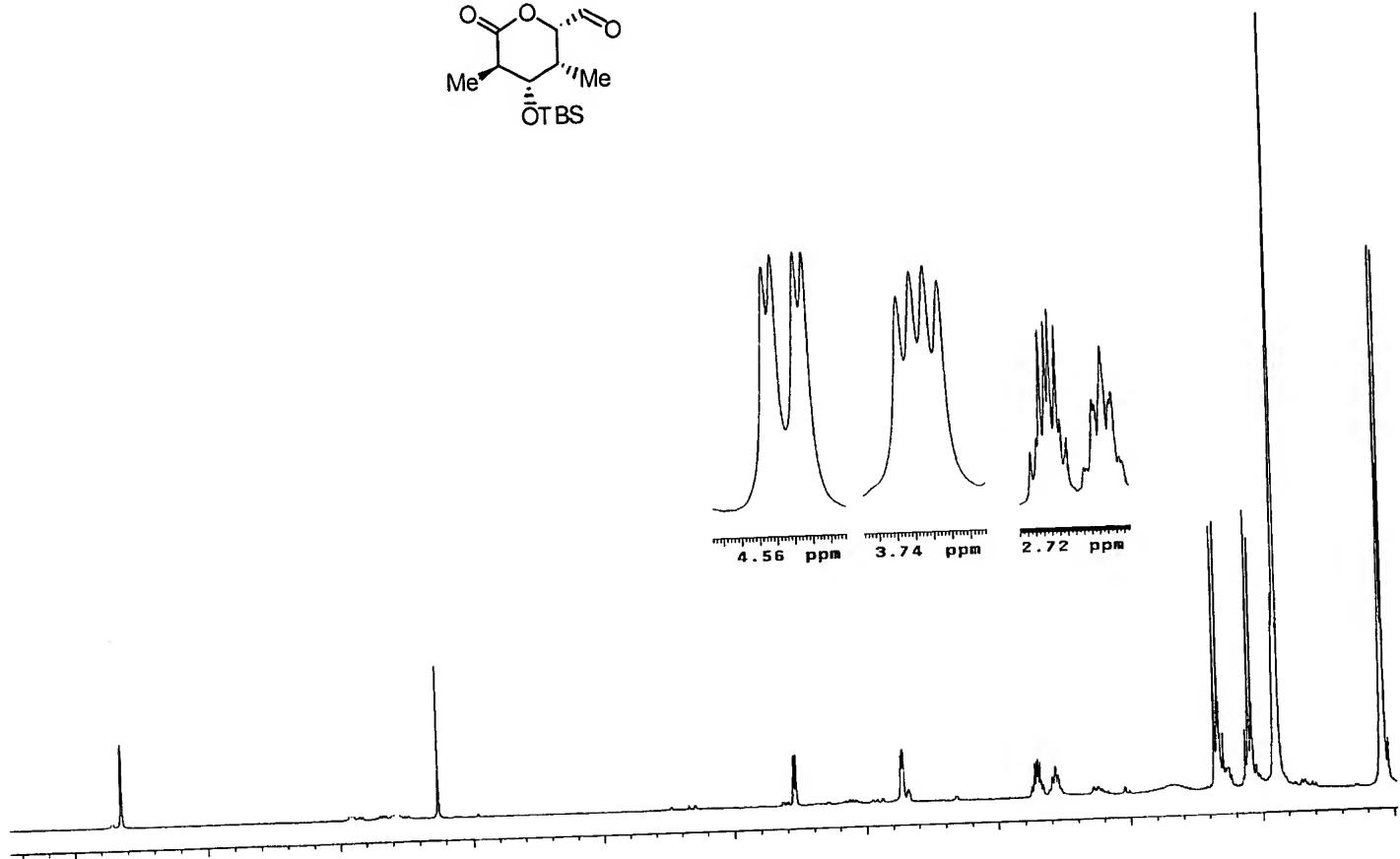
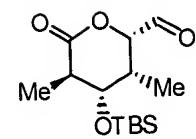
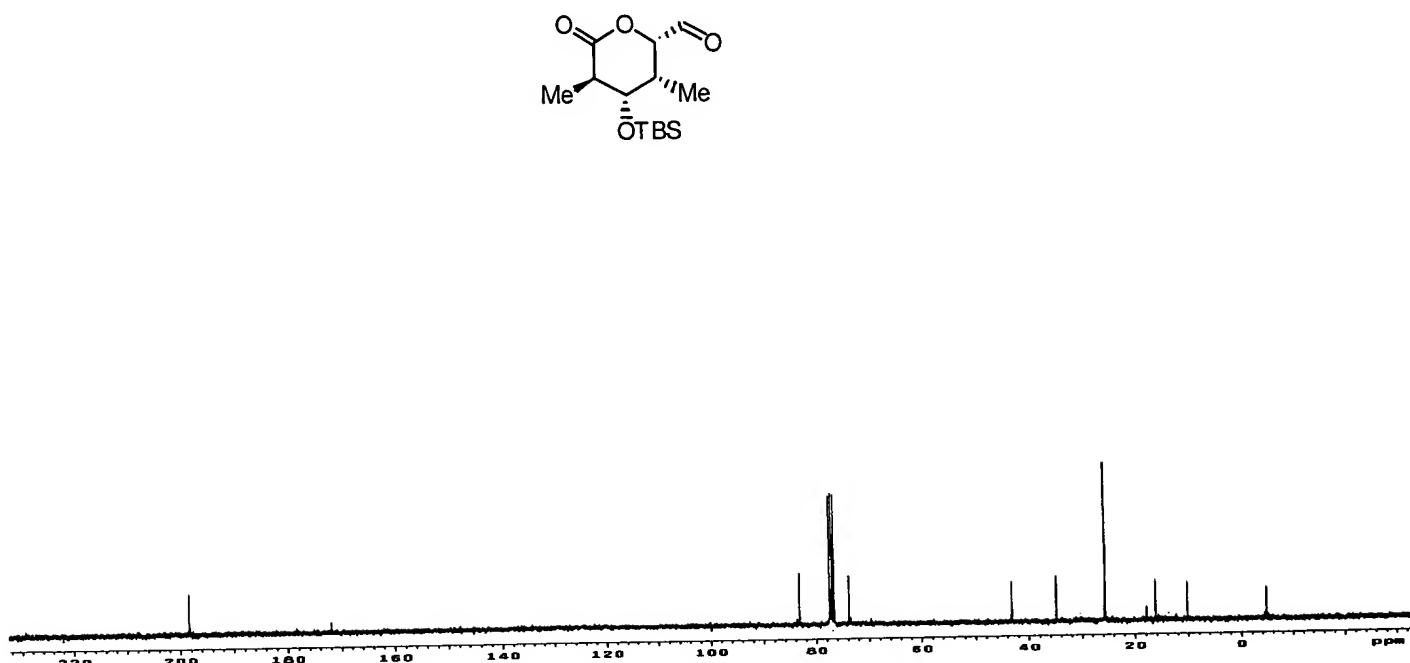


FIGURE 8 (99 Spectra)



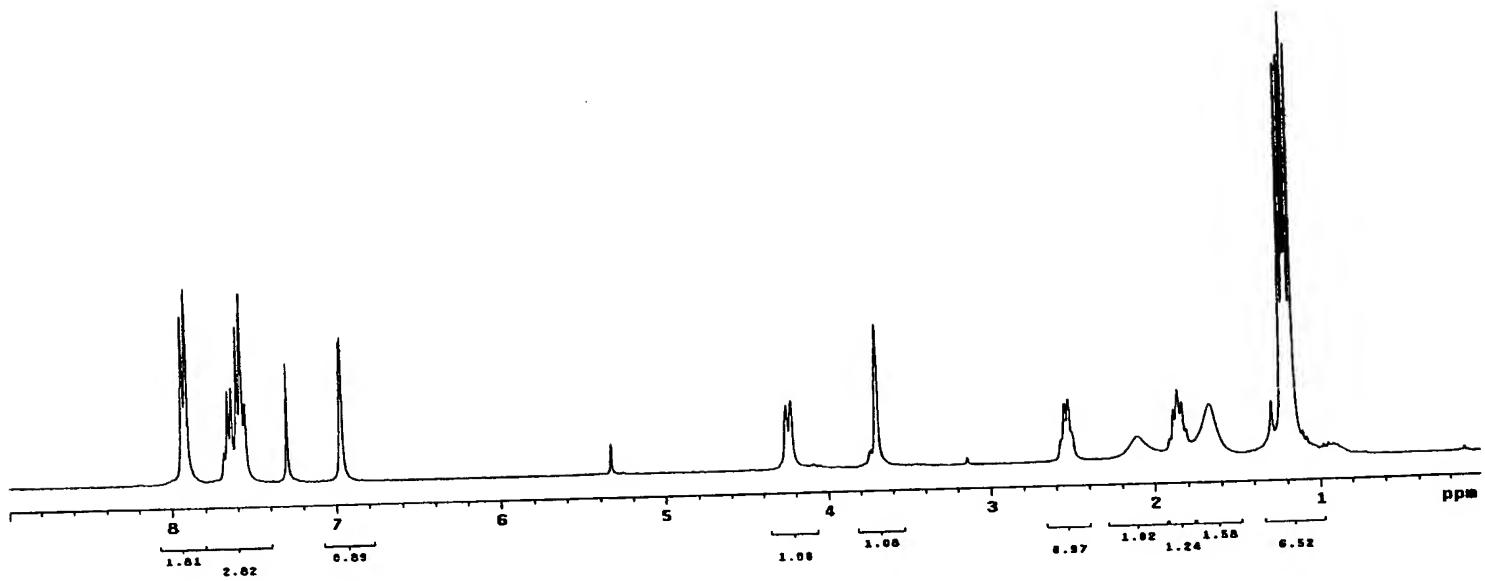
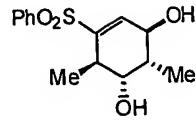
300MHz ^1H NMR of compound 22 in CDCl_3

FIGURE 8 (Cont'd)



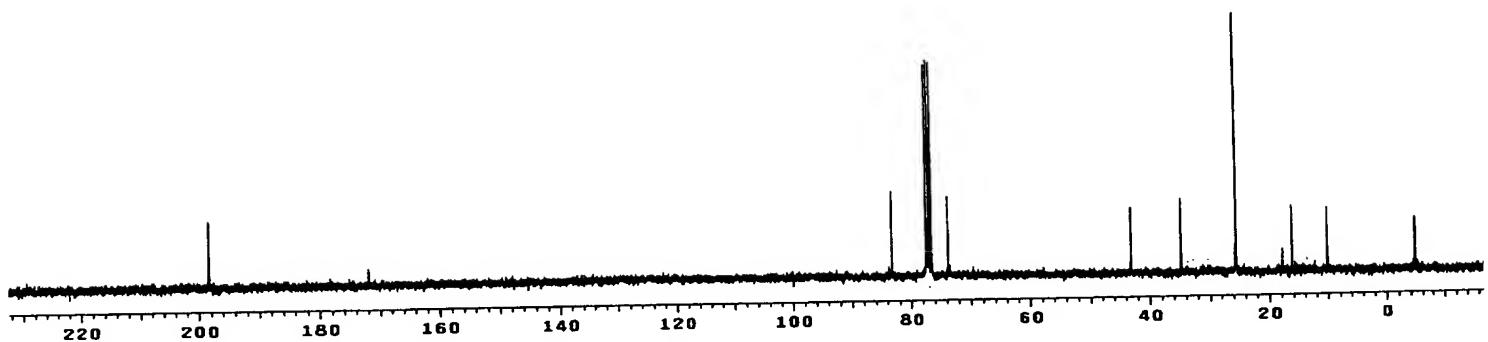
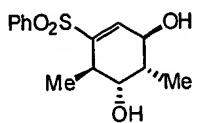
75MHz ^{13}C NMR of compound 22 in CDCl_3

FIGURE 8 (Cont'd)



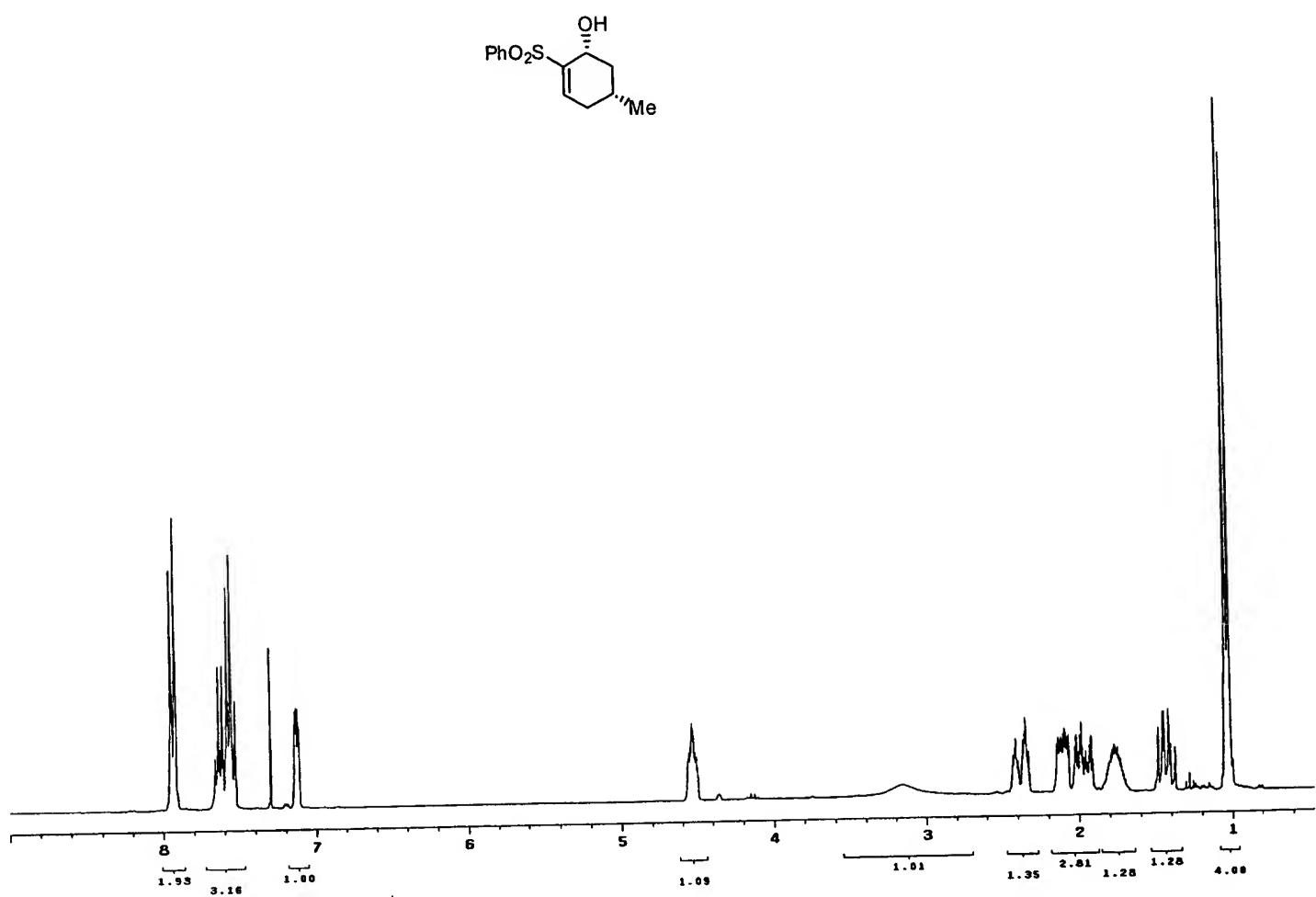
300MHz ^1H NMR of compound 23 in CDCl_3

FIGURE 8 (Cont'd)



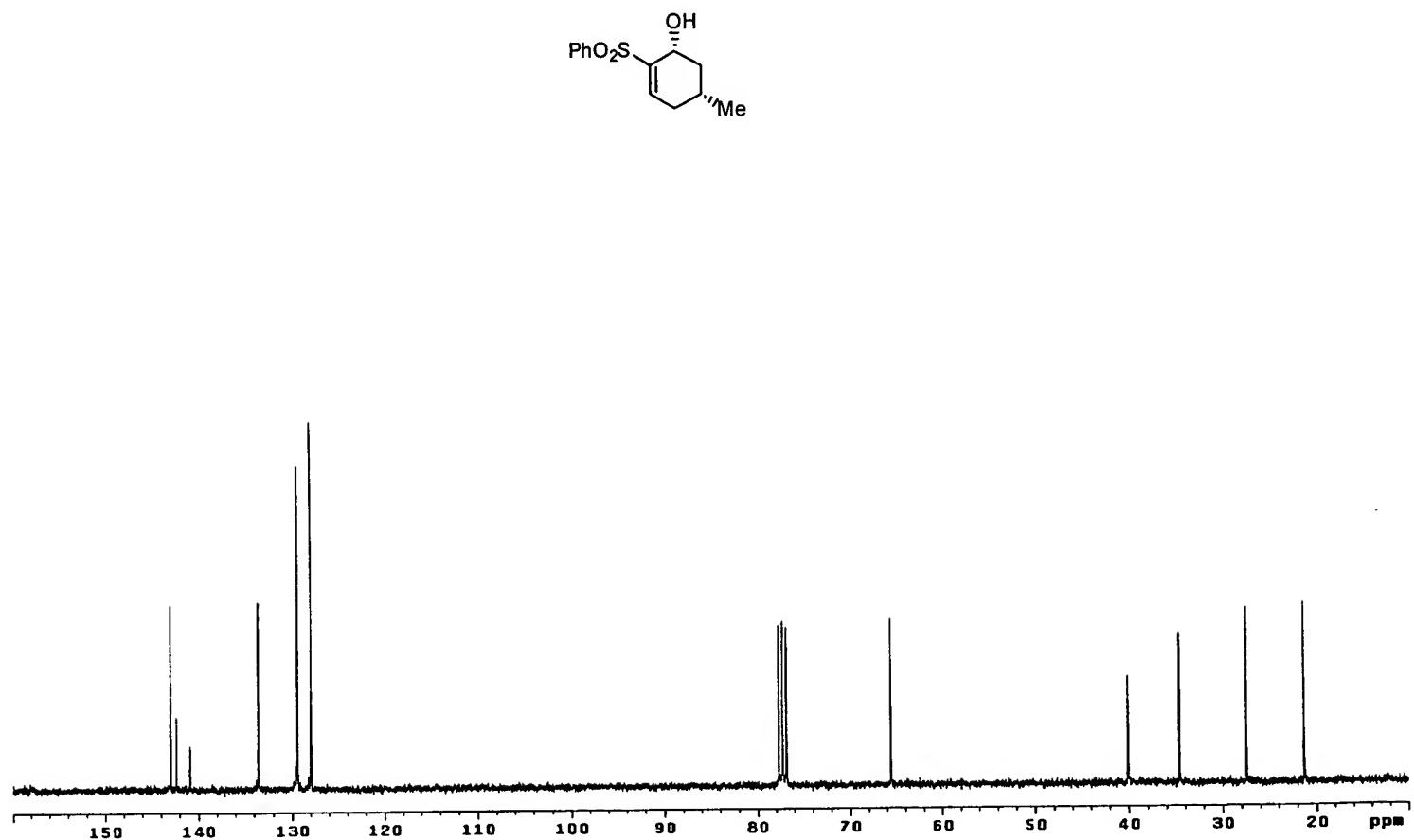
75MHz ^{13}C NMR of compound 23 in CDCl_3

FIGURE 8 (Cont'd)



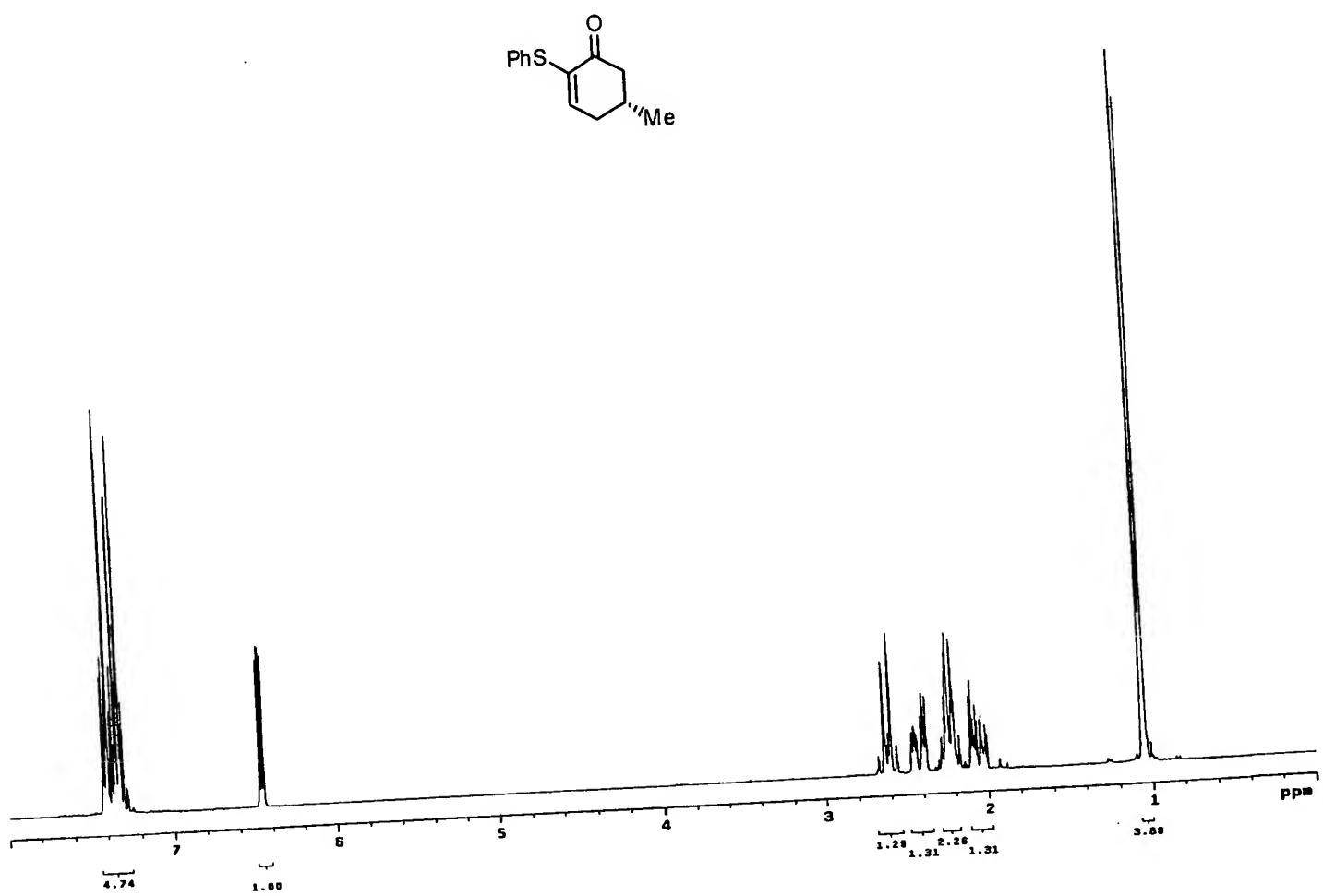
300MHz ^1H NMR of compound 24 in CDCl_3

FIGURE 8 (Cont'd)



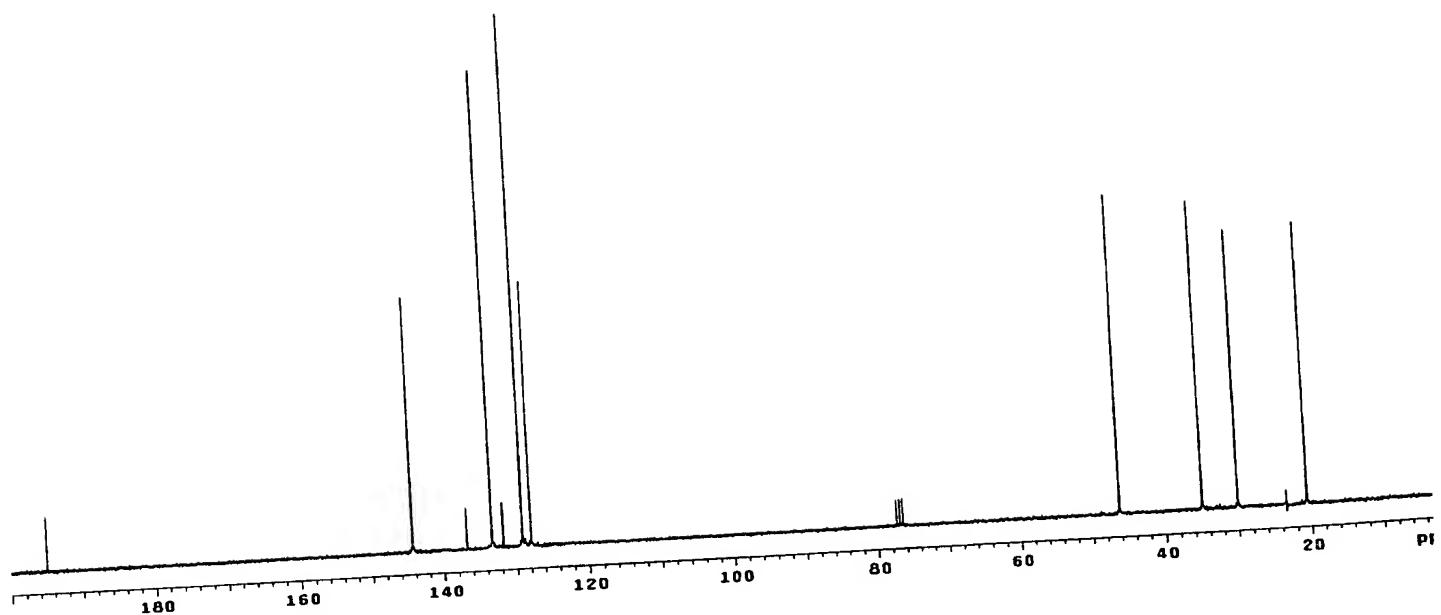
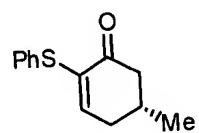
75MHz ^{13}C NMR of compound **24** in CDCl_3

FIGURE 8 (Cont'd)



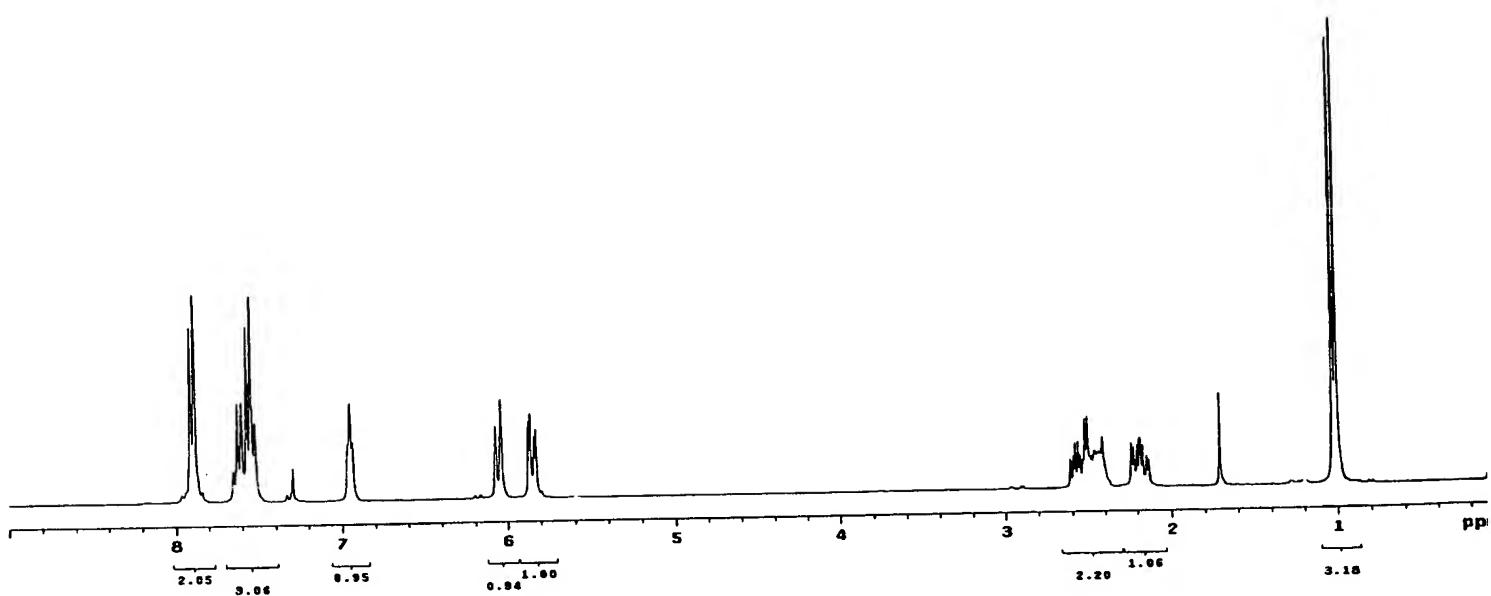
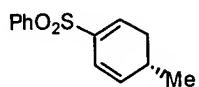
300MHz ^1H NMR of compound **28** in CDCl_3

FIGURE 8 (Cont'd)



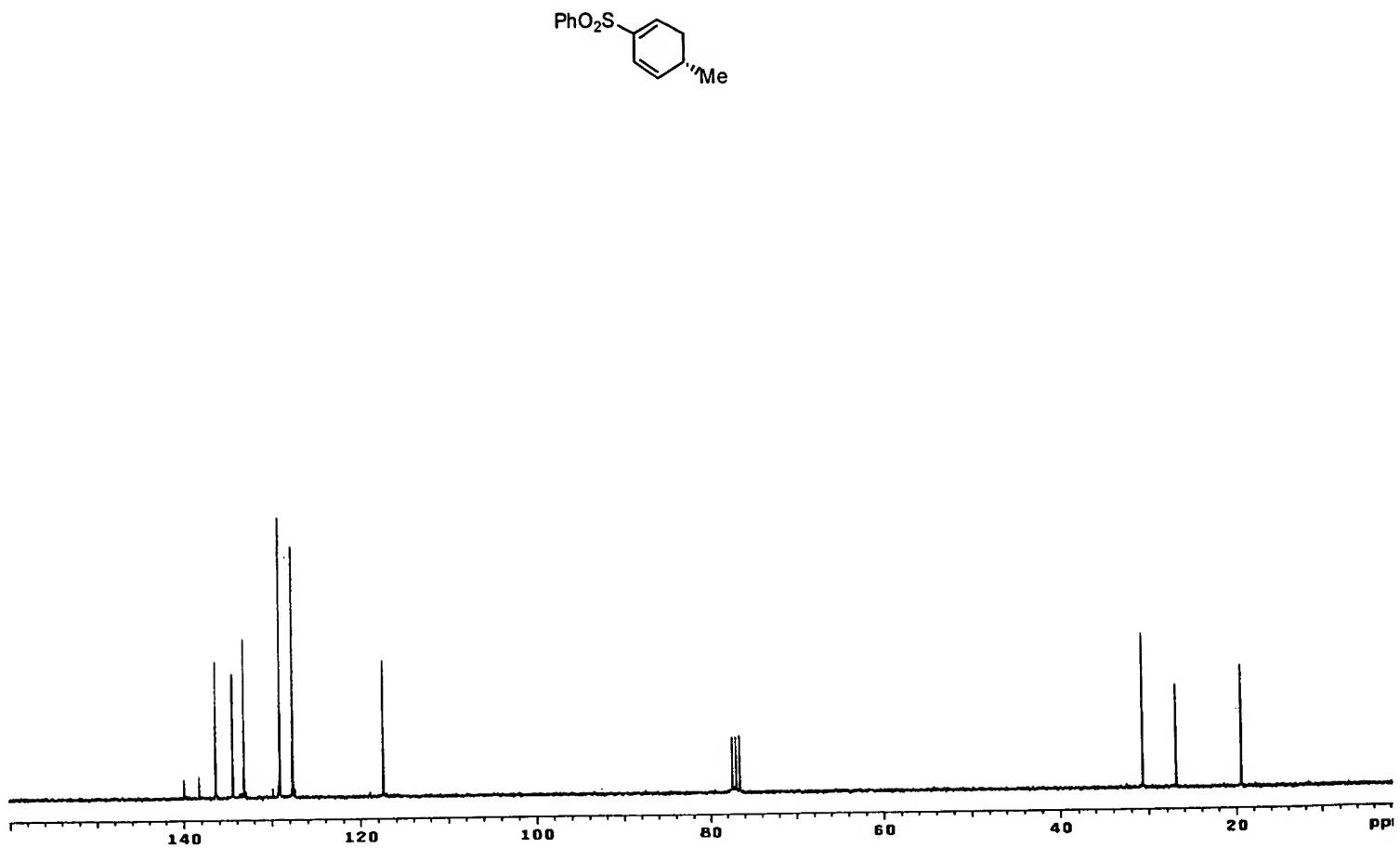
75MHz ^{13}C NMR of compound **28** in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound **29** in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 29 in CDCl_3

FIGURE 8 (Cont'd)

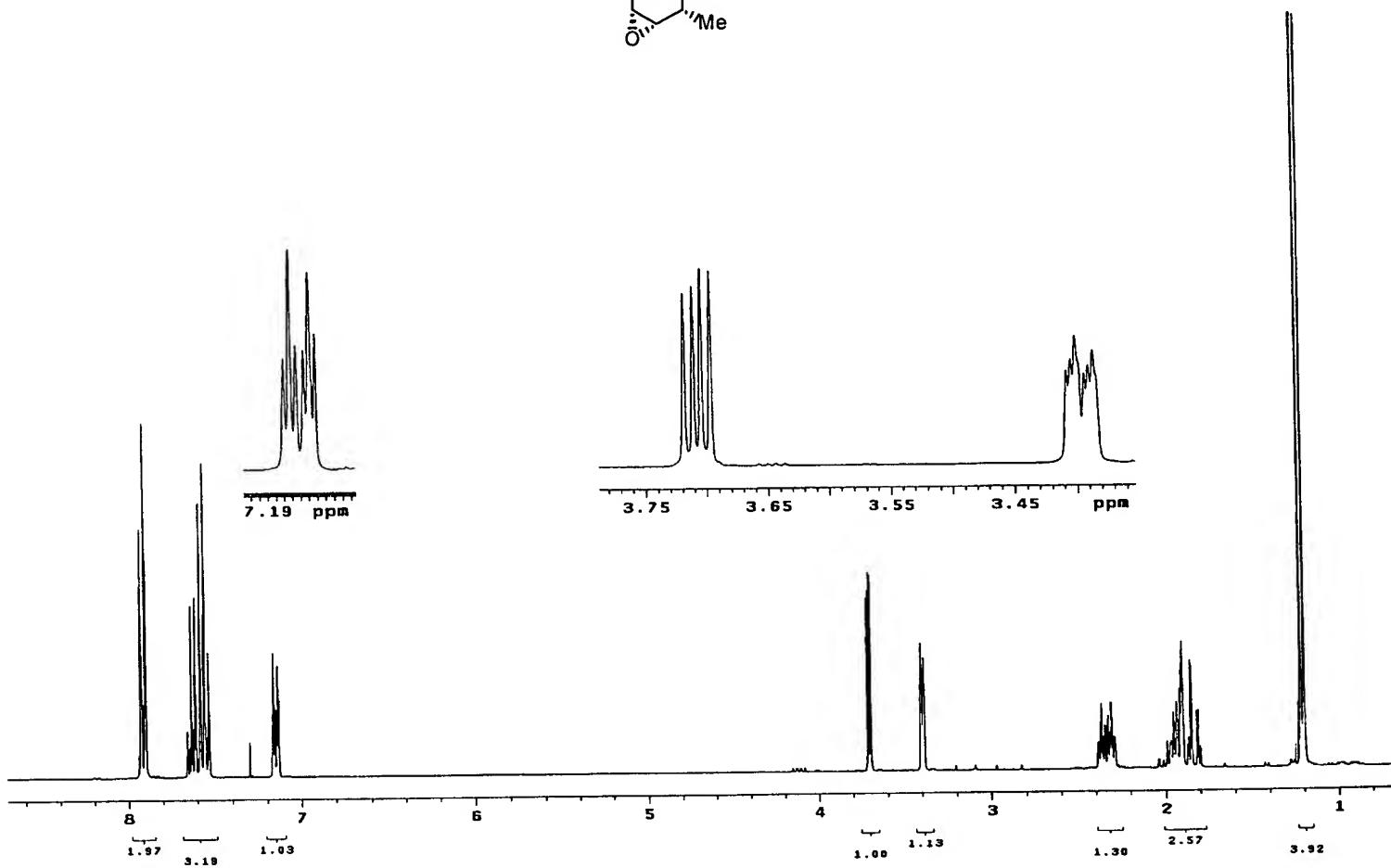
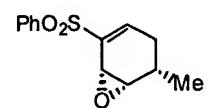
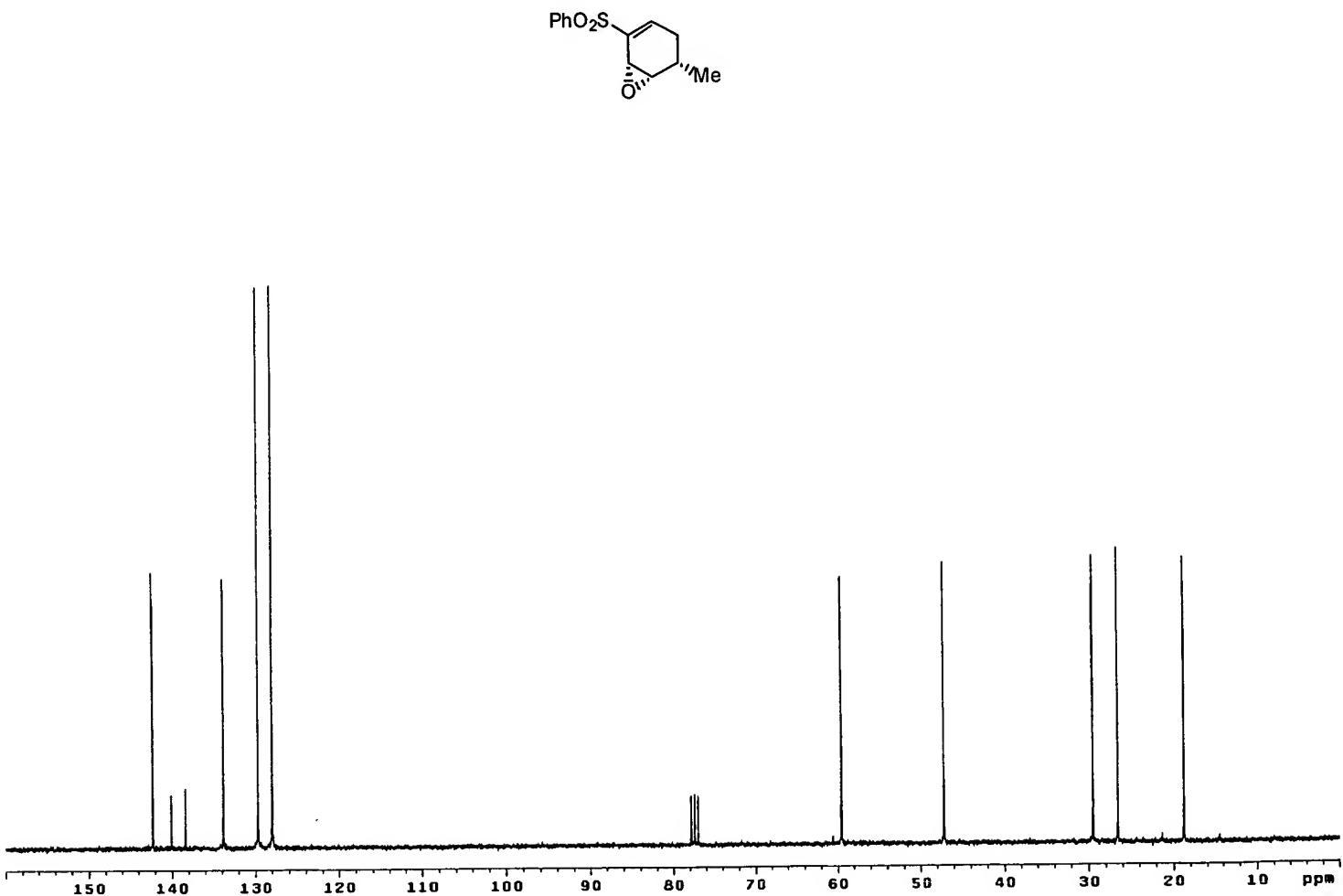
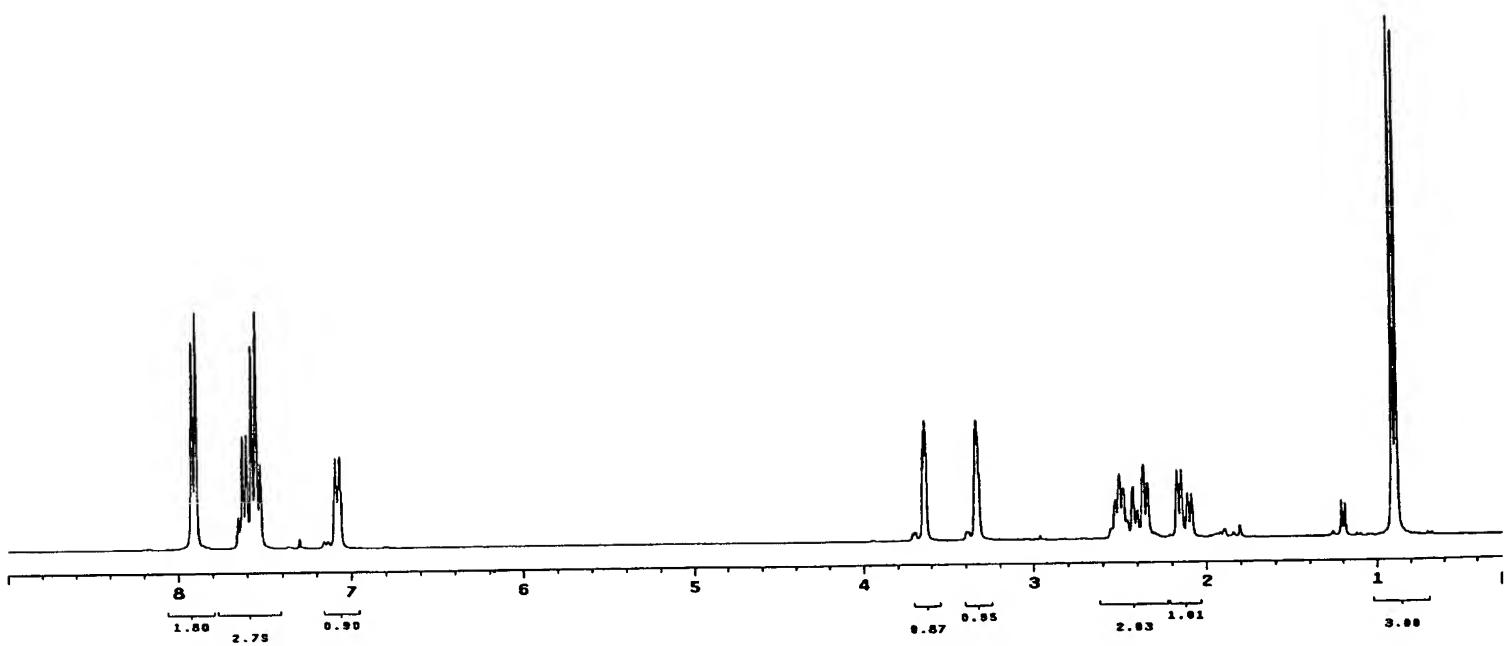
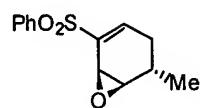


FIGURE 8 (Cont'd)



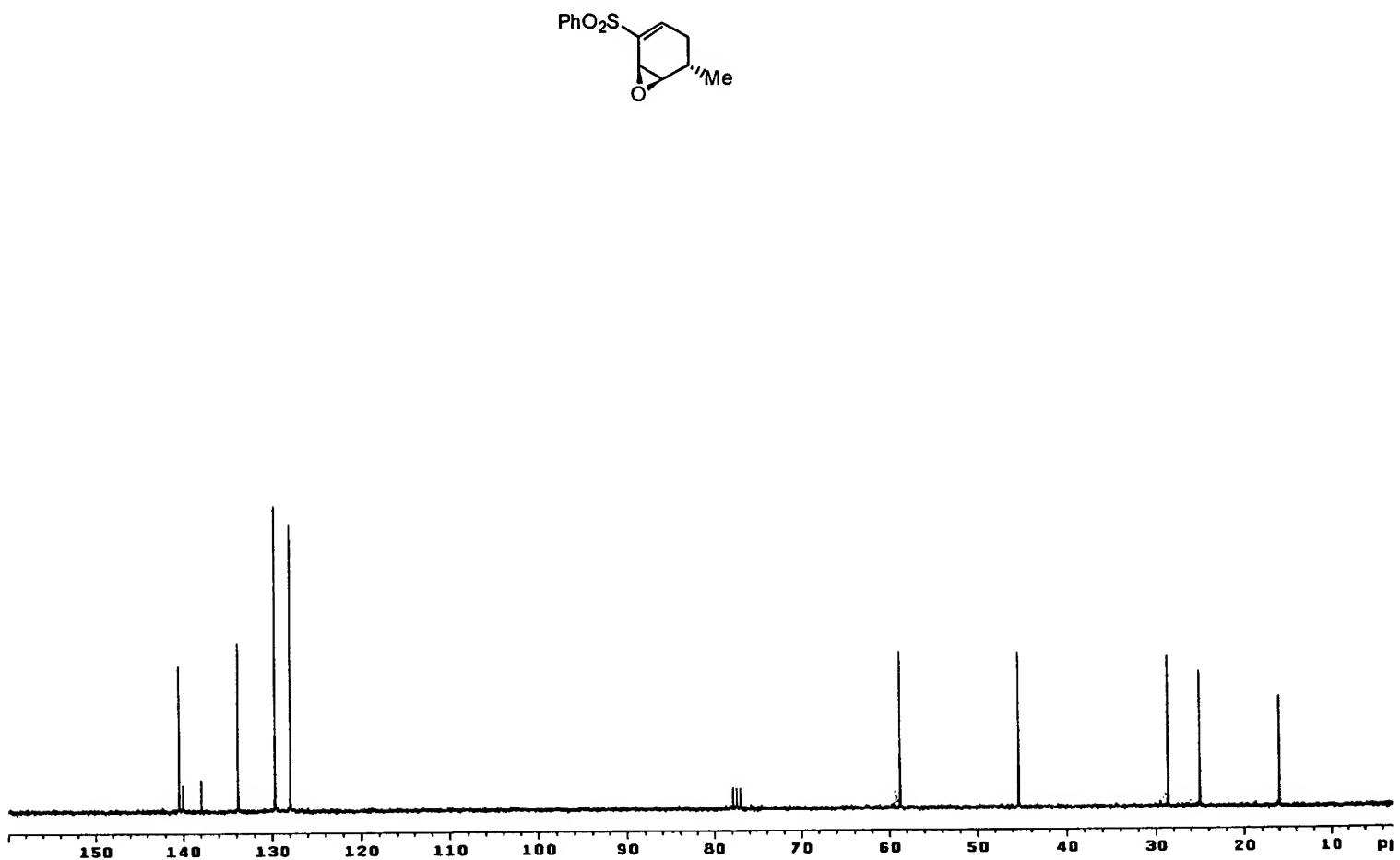
75MHz ^{13}C NMR of compound **30** in CDCl_3

FIGURE 8 (Cont'd)



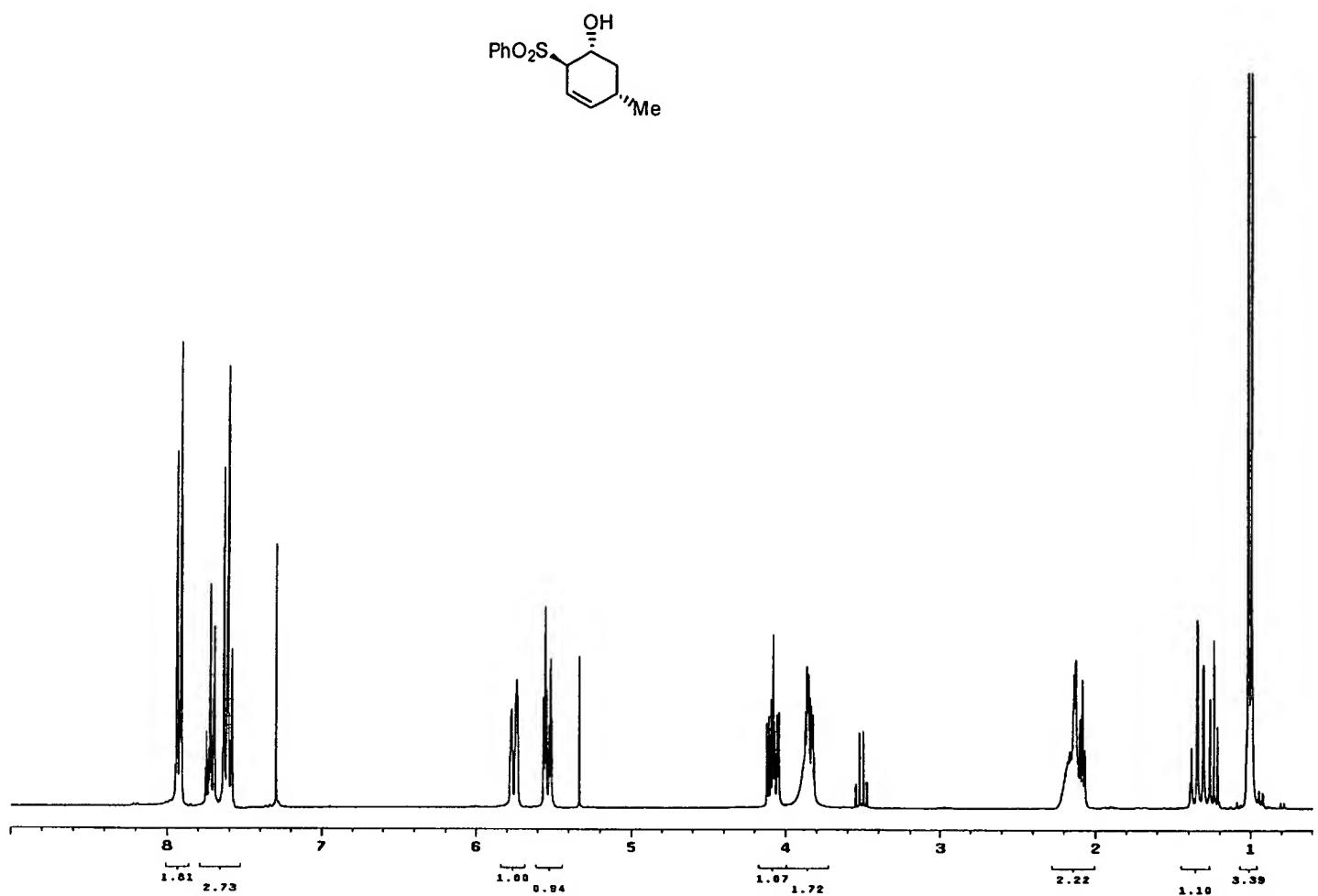
300MHz ^1H NMR of compound **31** in CDCl_3

FIGURE 8 (Cont'd)



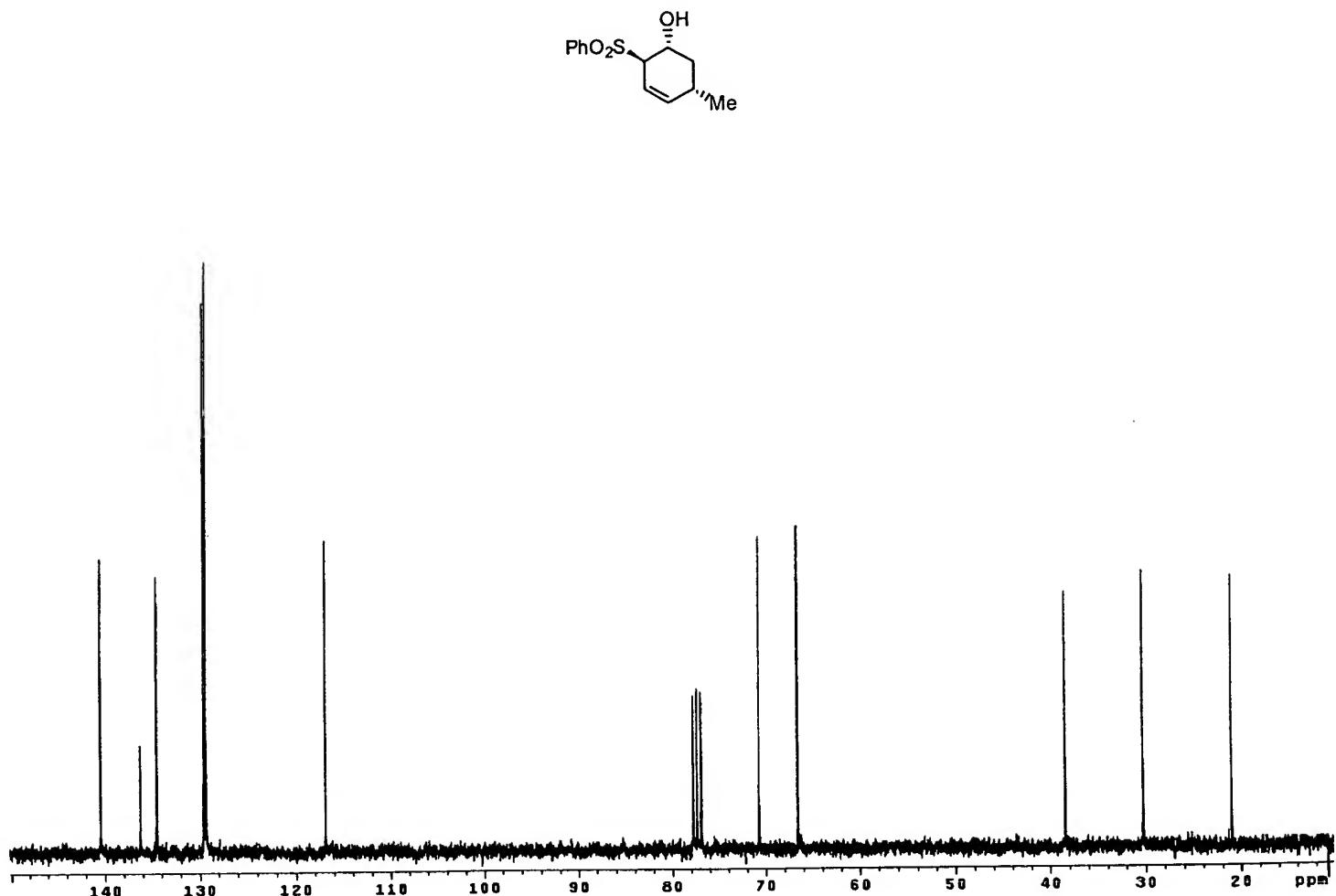
75MHz ^{13}C NMR of compound **31** in CDCl_3

FIGURE 8 (Cont'd)



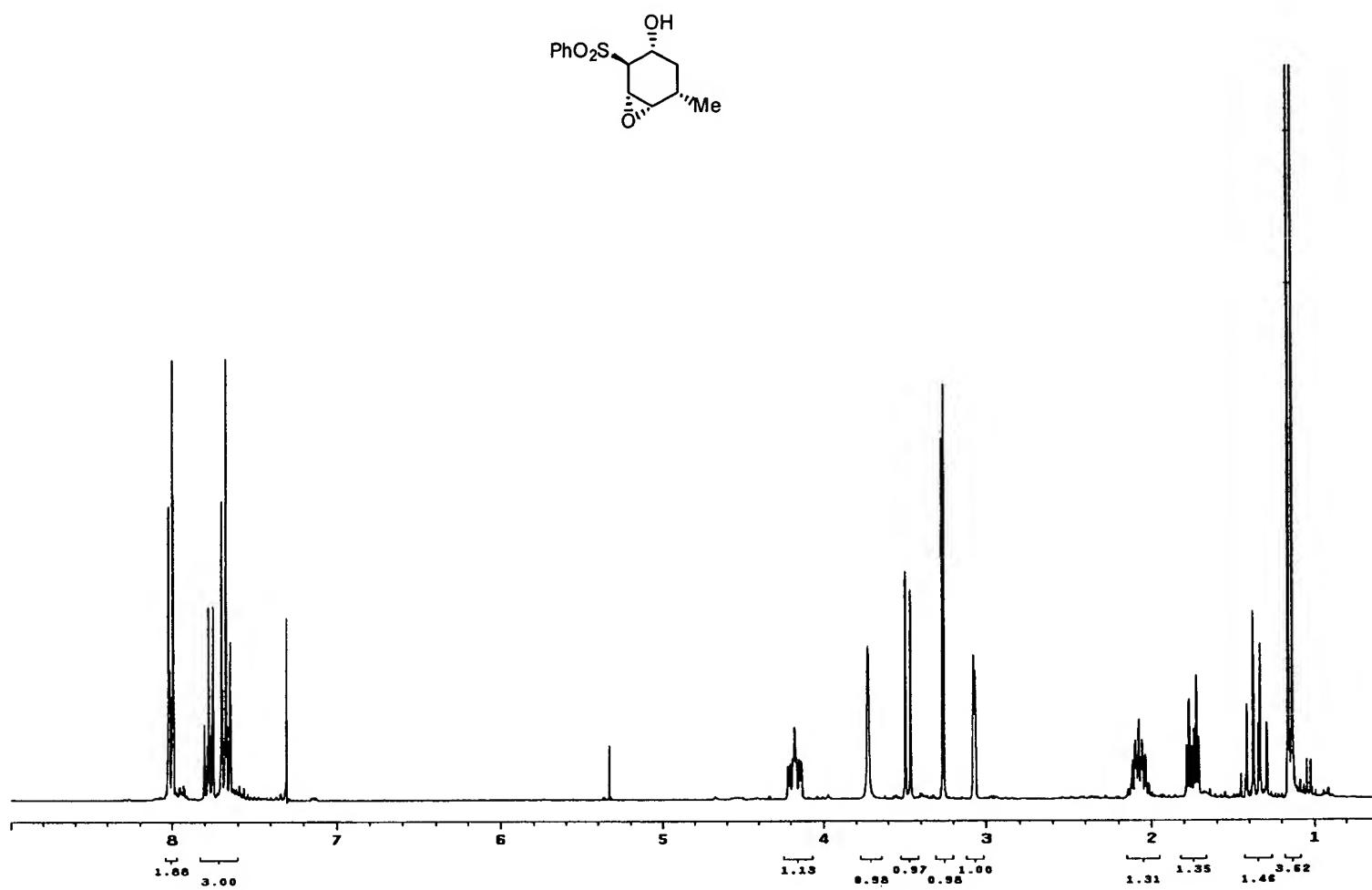
300MHz ^1H NMR of compound **32** in CDCl_3

FIGURE 8 (Cont'd)



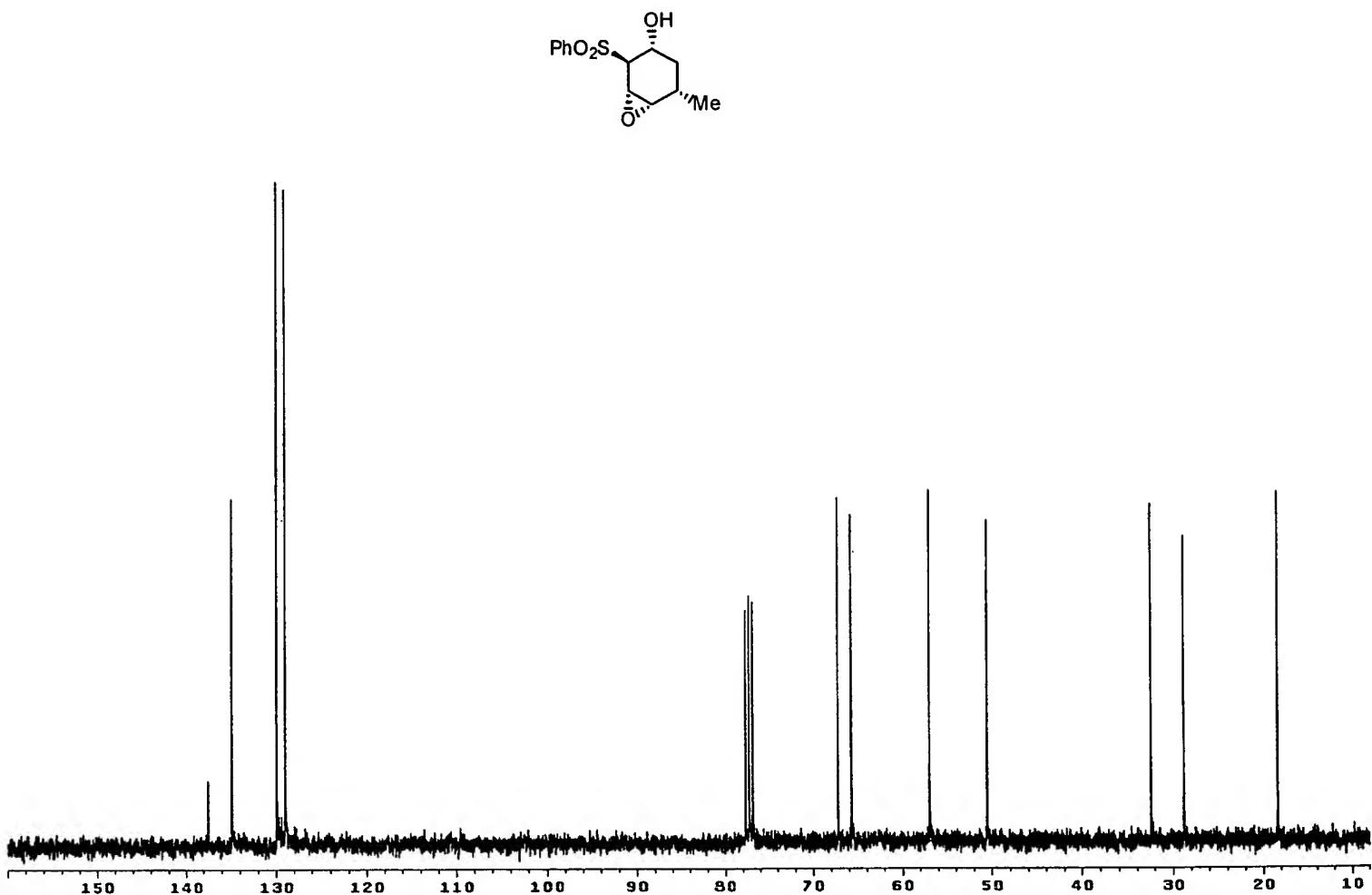
75MHz ^{13}C NMR of compound **32** in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 33 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound **33** in CDCl_3

FIGURE 8 (Cont'd)

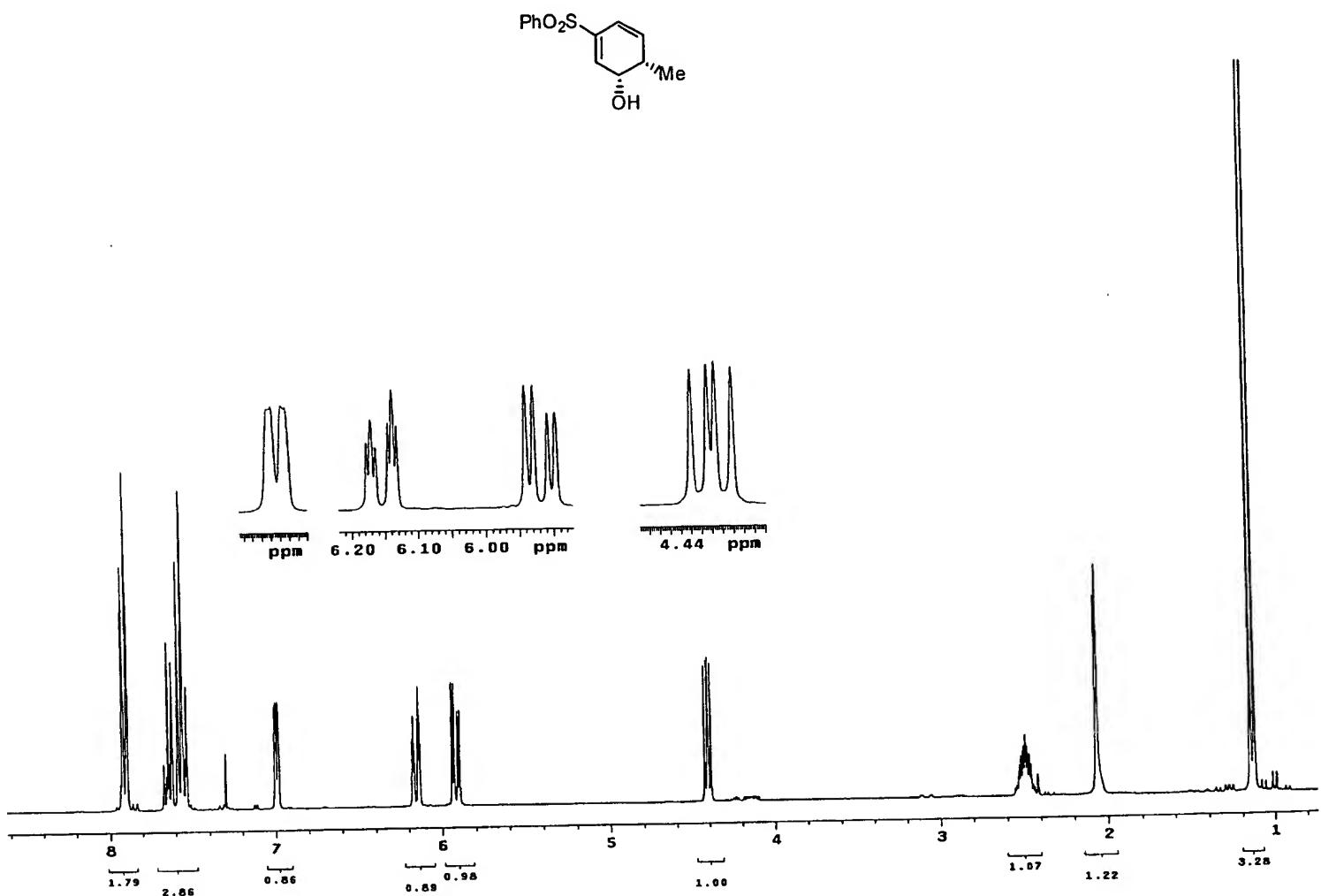
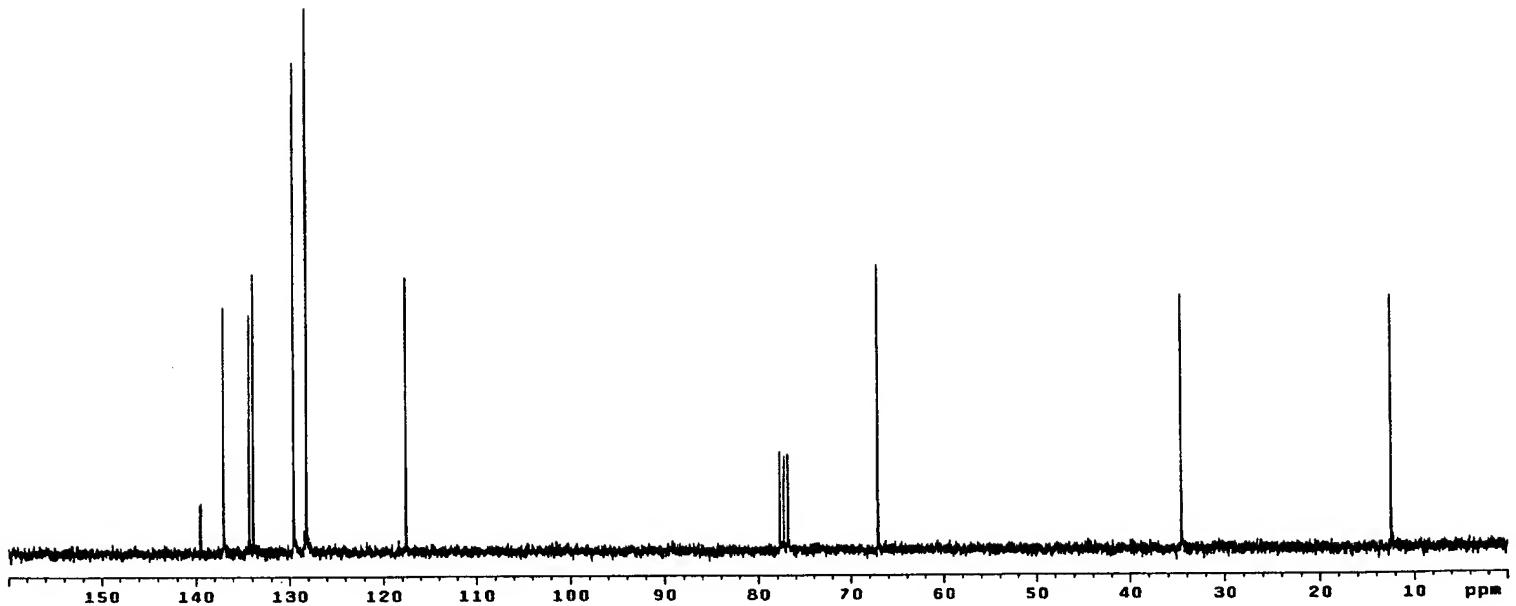
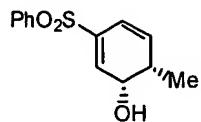
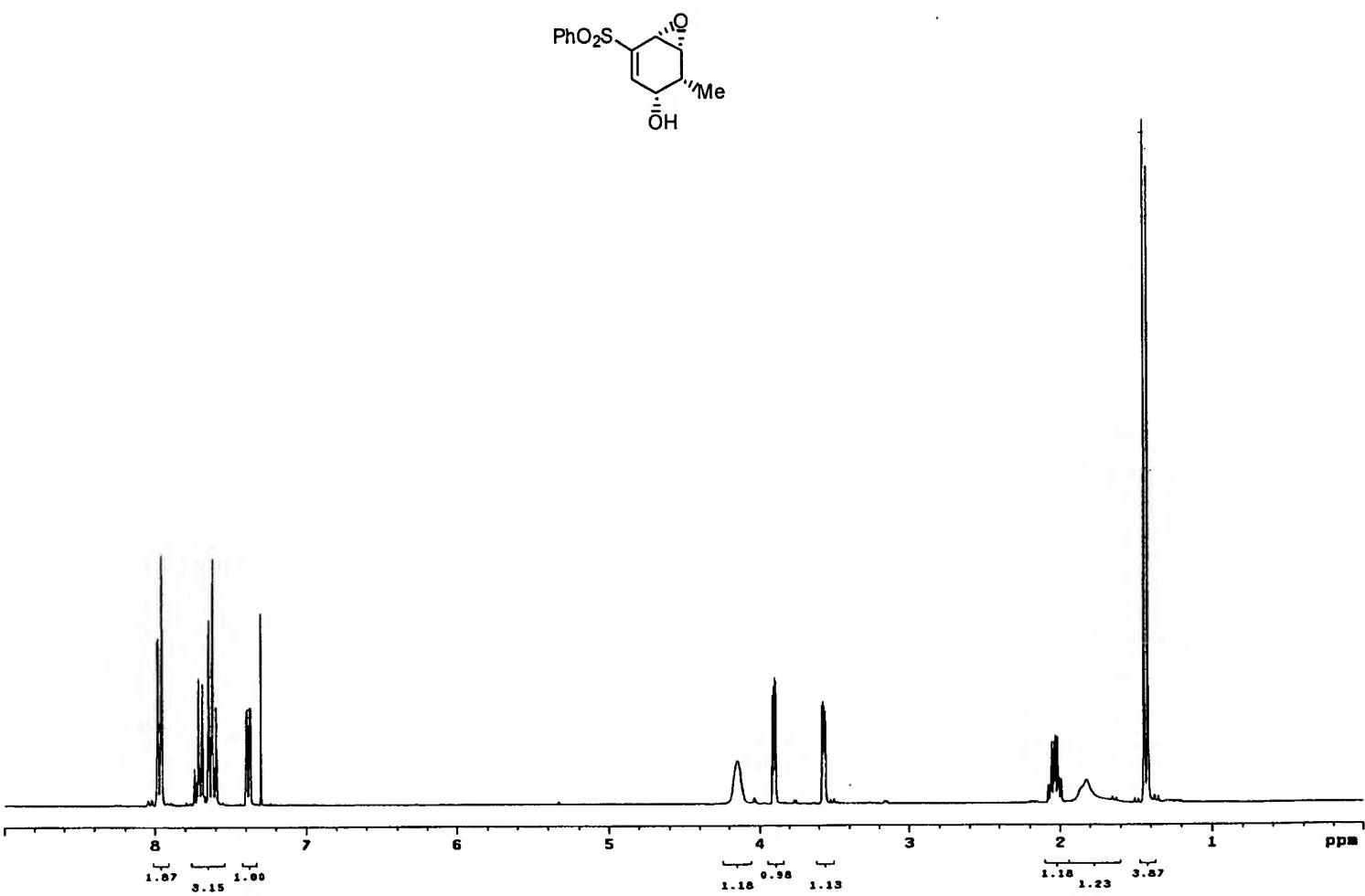


FIGURE 8 (Cont'd)



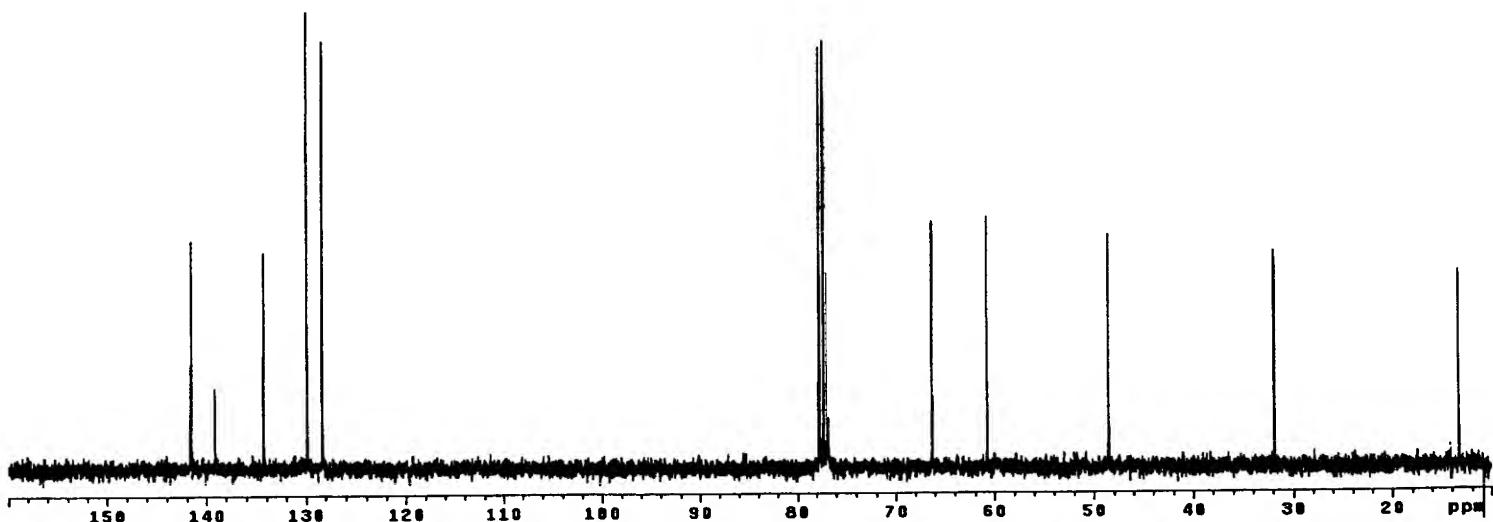
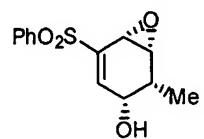
75MHz ^{13}C NMR of compound **35** in CDCl_3

FIGURE 8 (Cont'd)



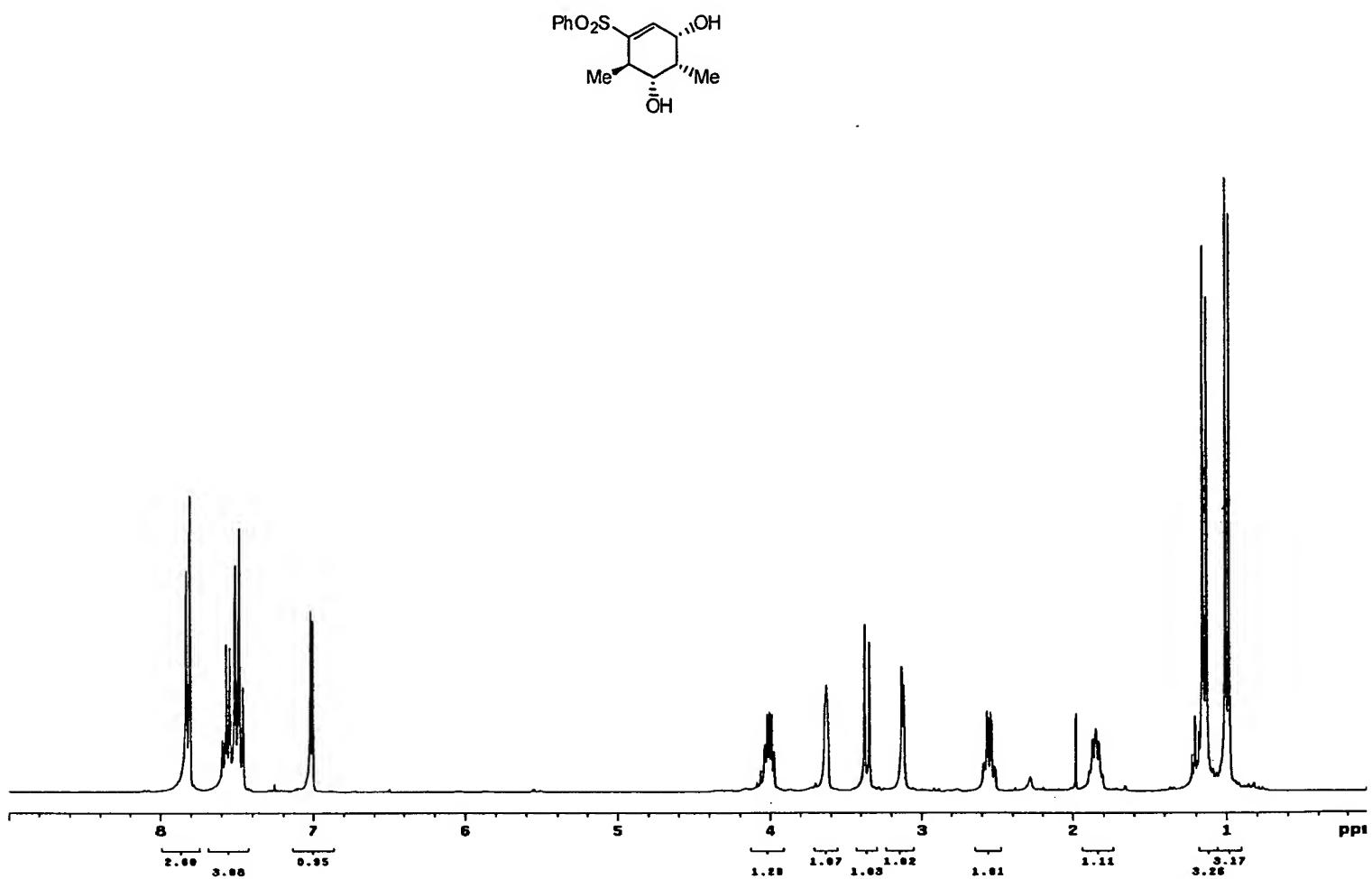
300MHz ^1H NMR of compound 36 in CDCl_3

FIGURE 8 (Cont'd)



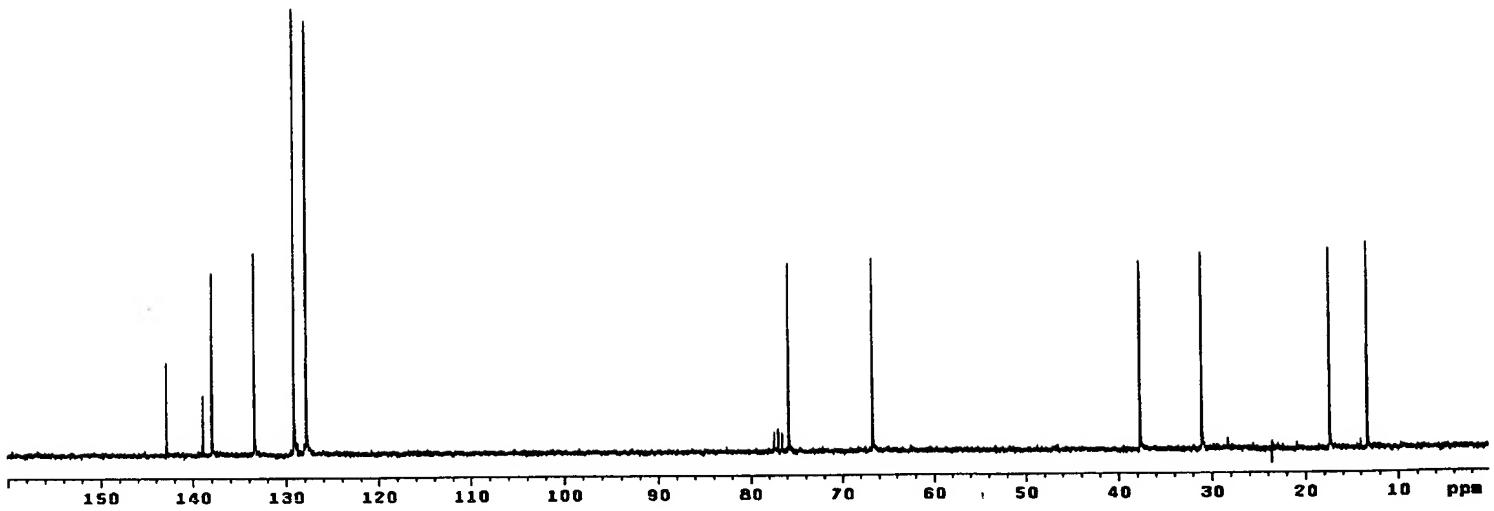
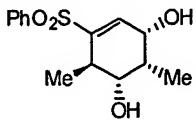
75MHz ^{13}C NMR of compound 36 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 37 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 37 in CDCl_3

FIGURE 8 (Cont'd)

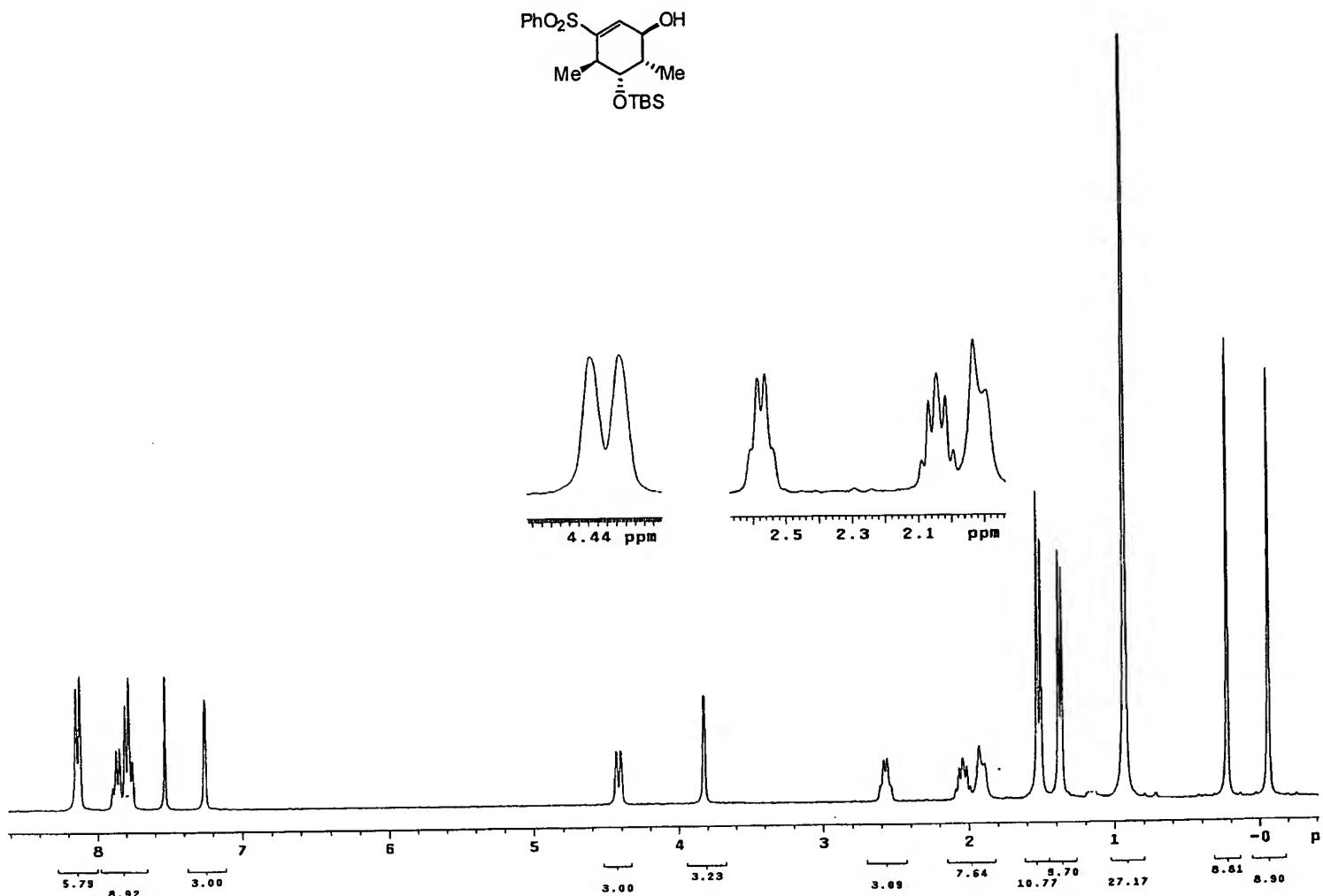
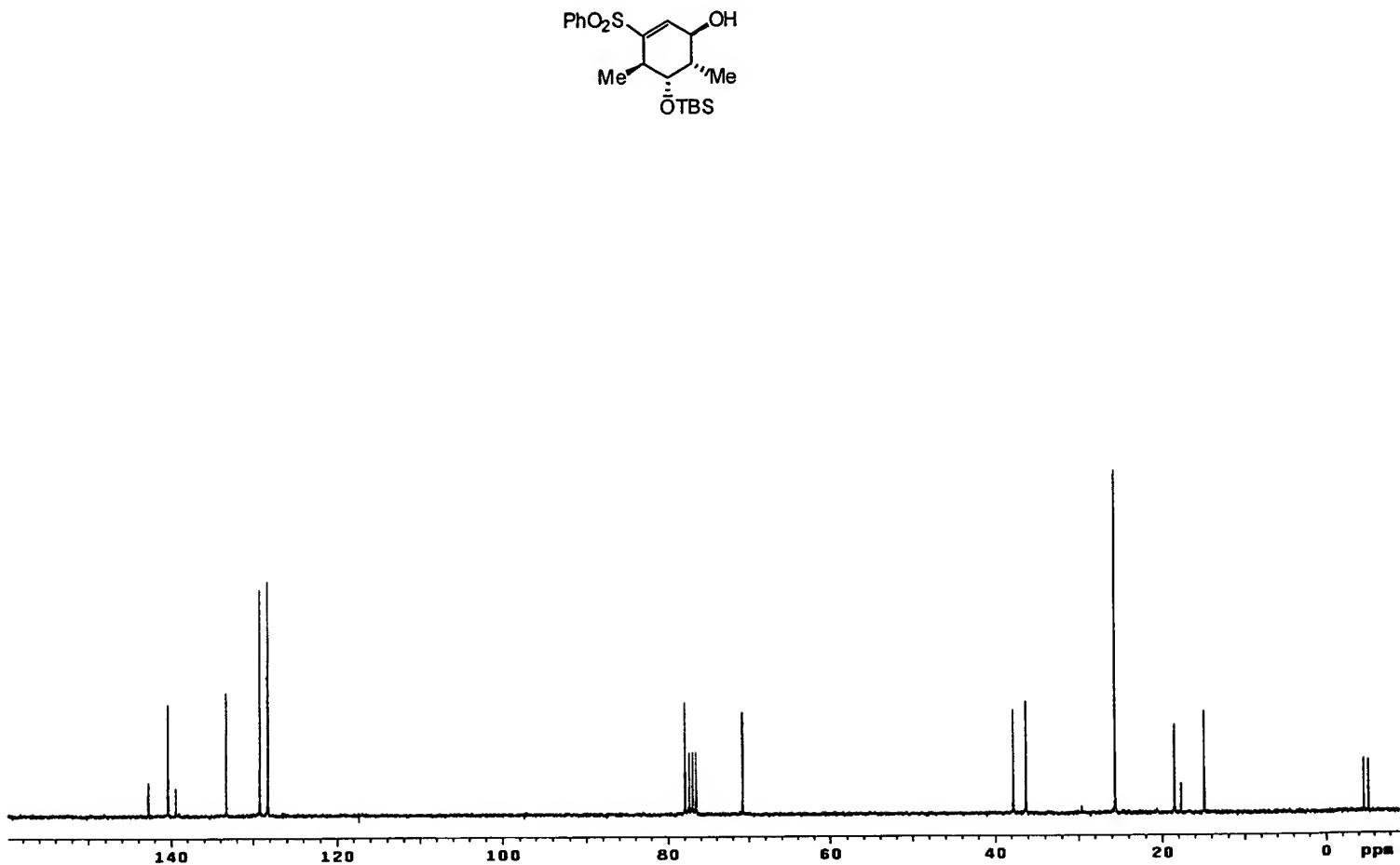


FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 38 in CDCl_3

FIGURE 8 (Cont'd)

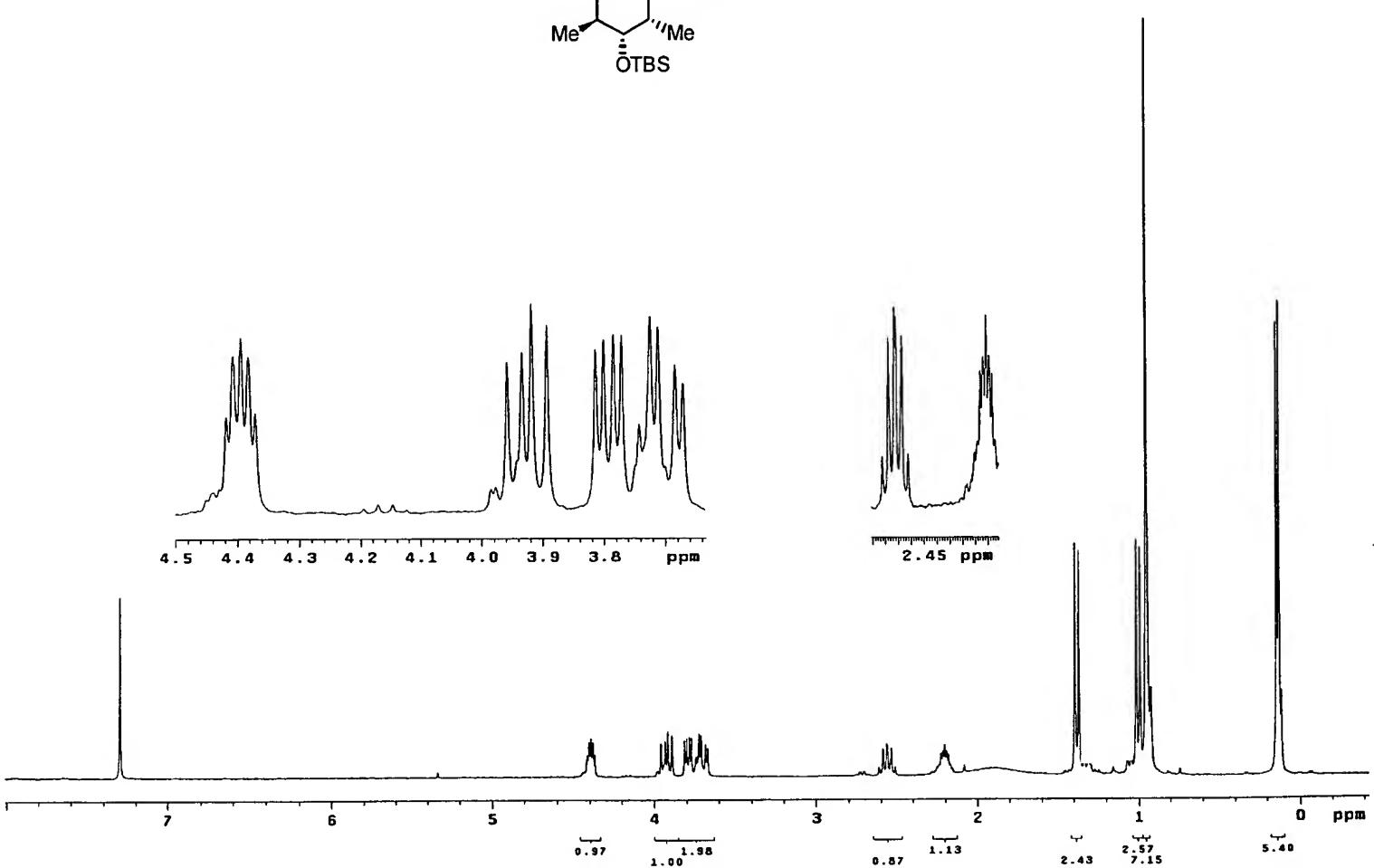
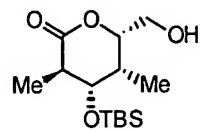
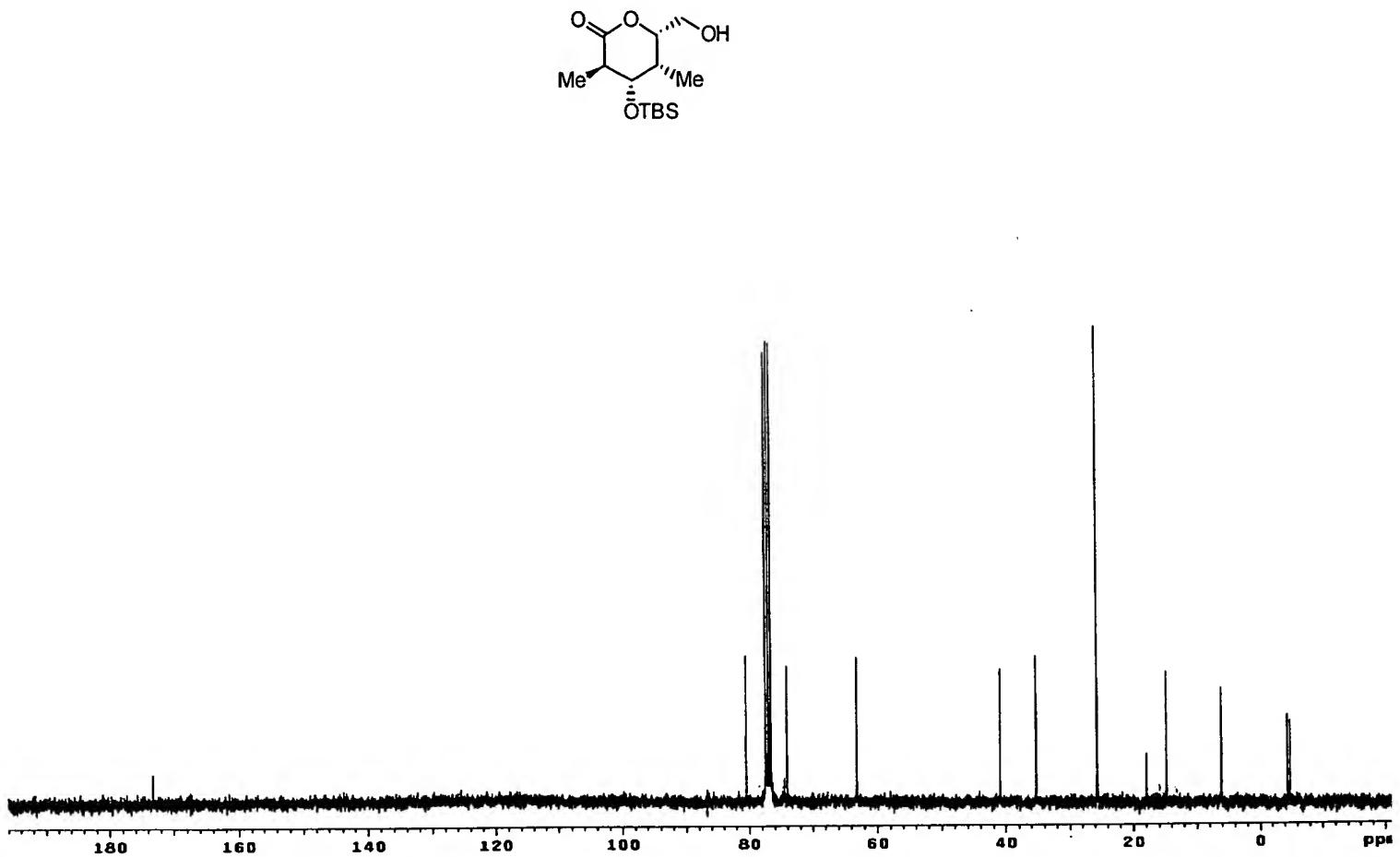
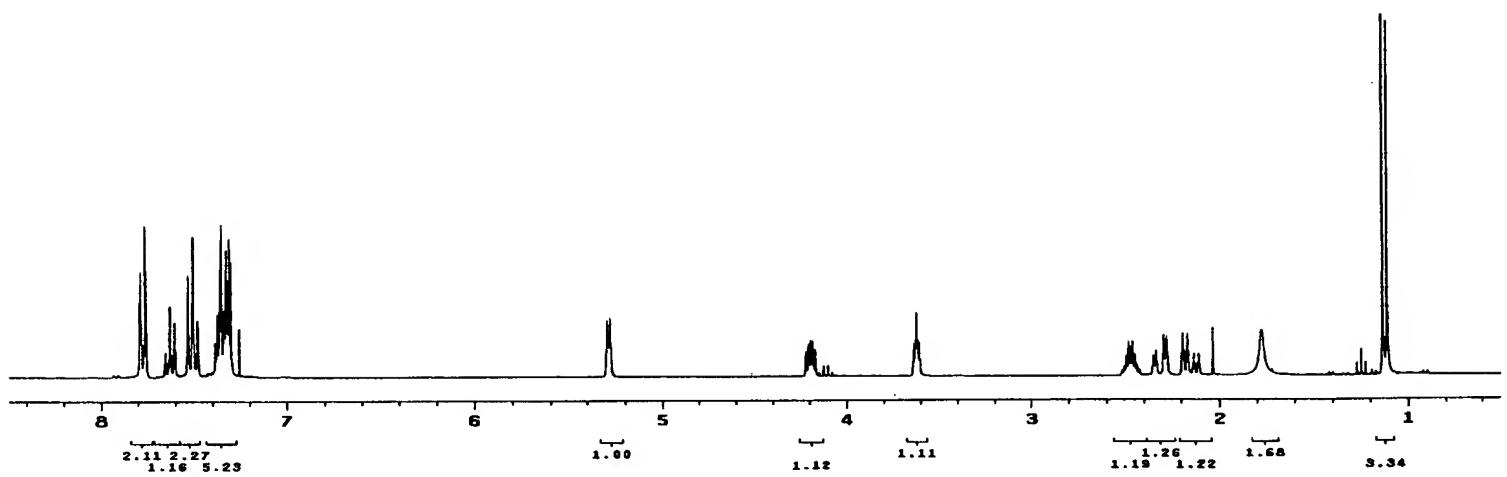
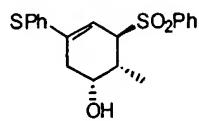


FIGURE 8 (Cont'd)



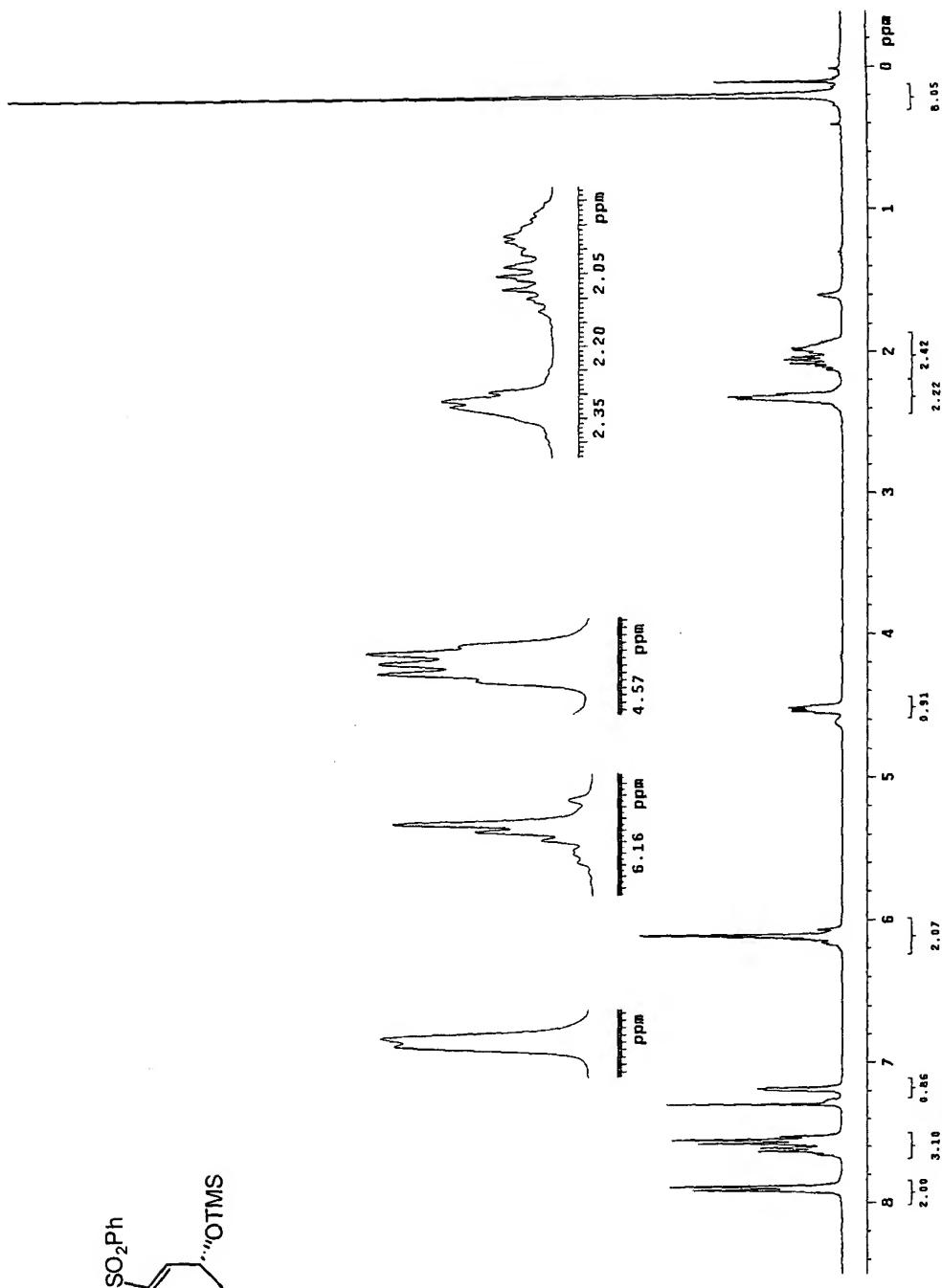
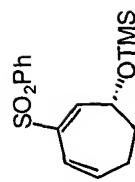
75MHz ^{13}C NMR of compound 39 in CDCl_3

FIGURE 8 (Cont'd)



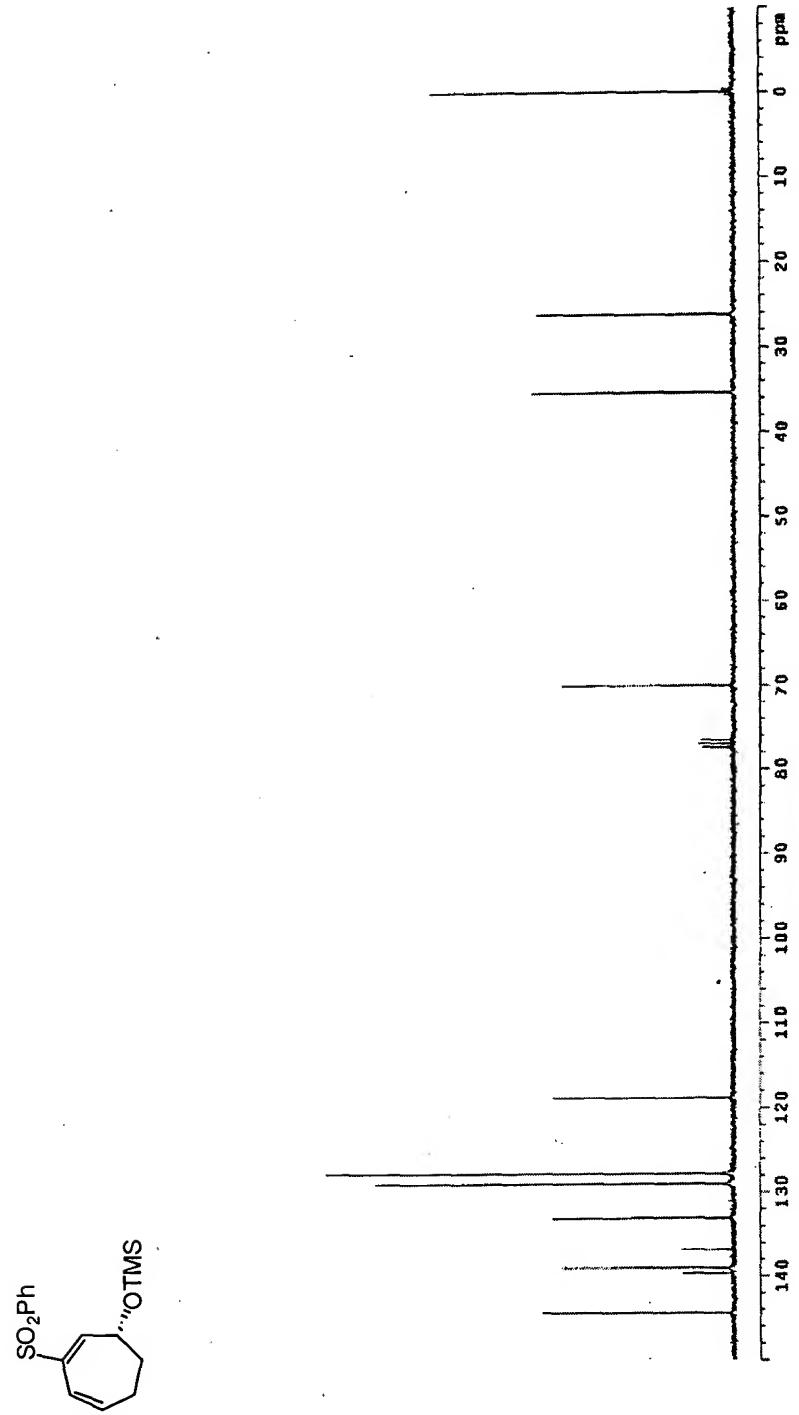
300MHz ^1H NMR of compound **43 β** in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 13 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 13 in CDCl_3

FIGURE 8 (Cont'd)

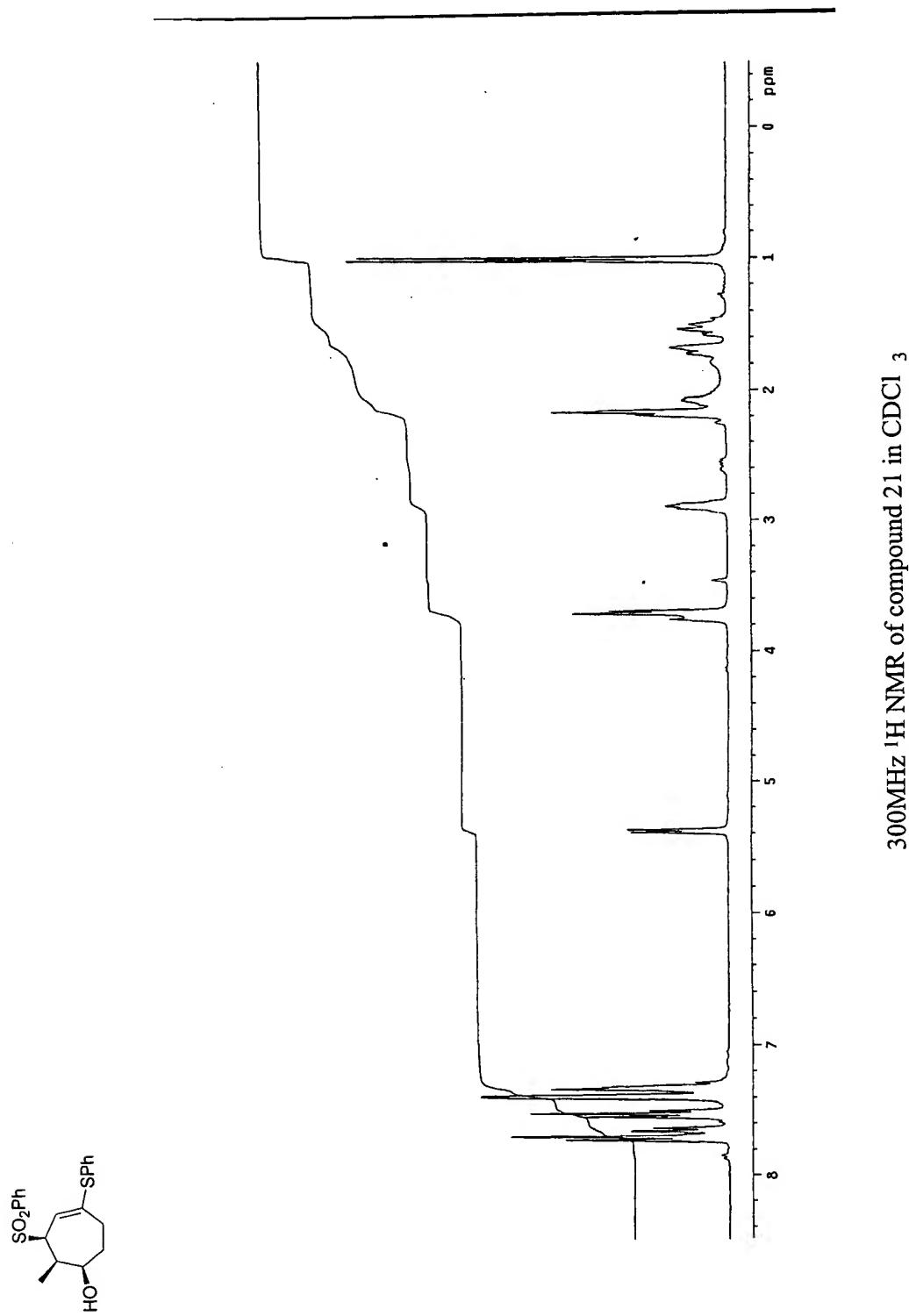


FIGURE 8 (Cont'd)

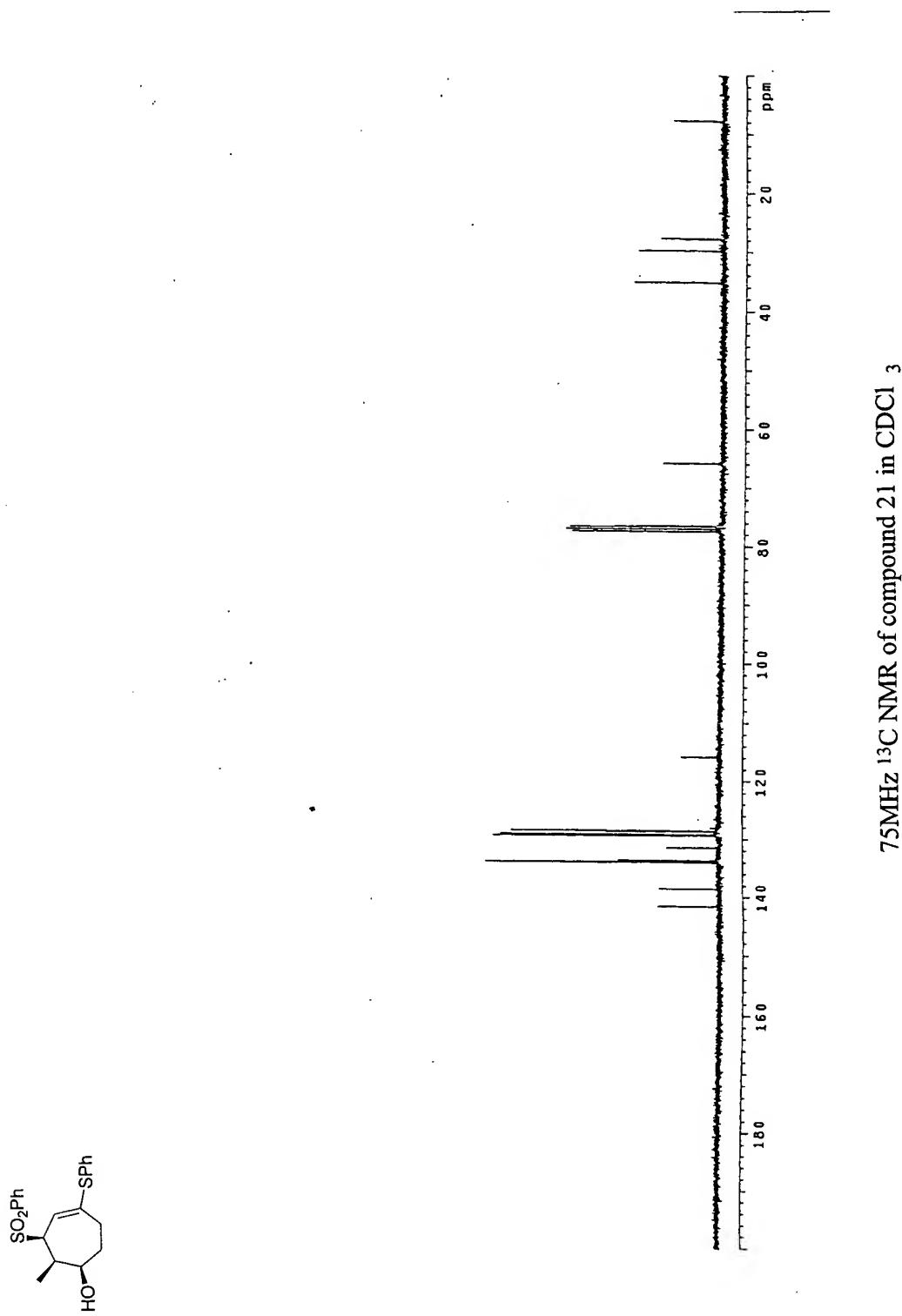
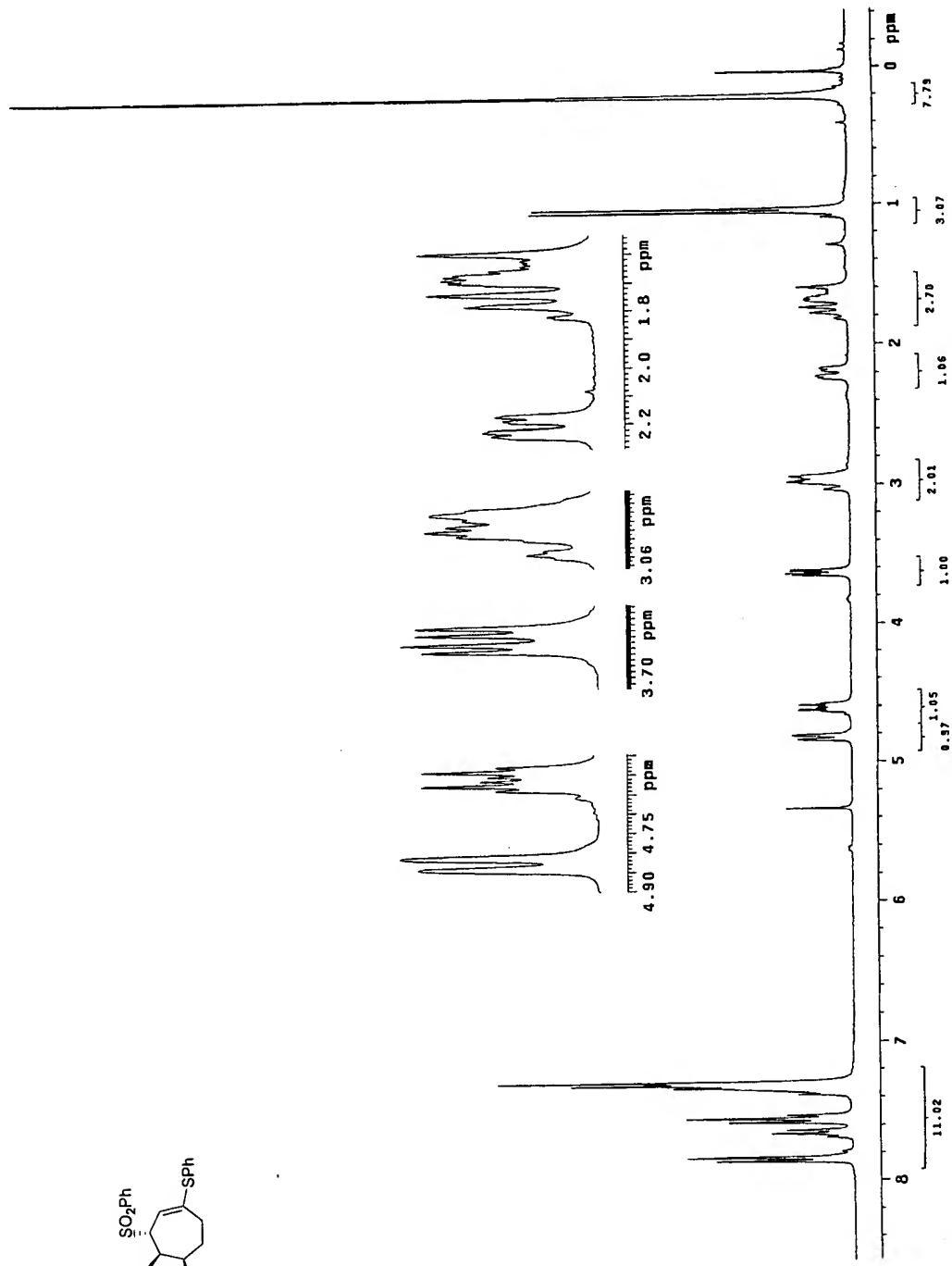
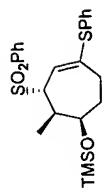
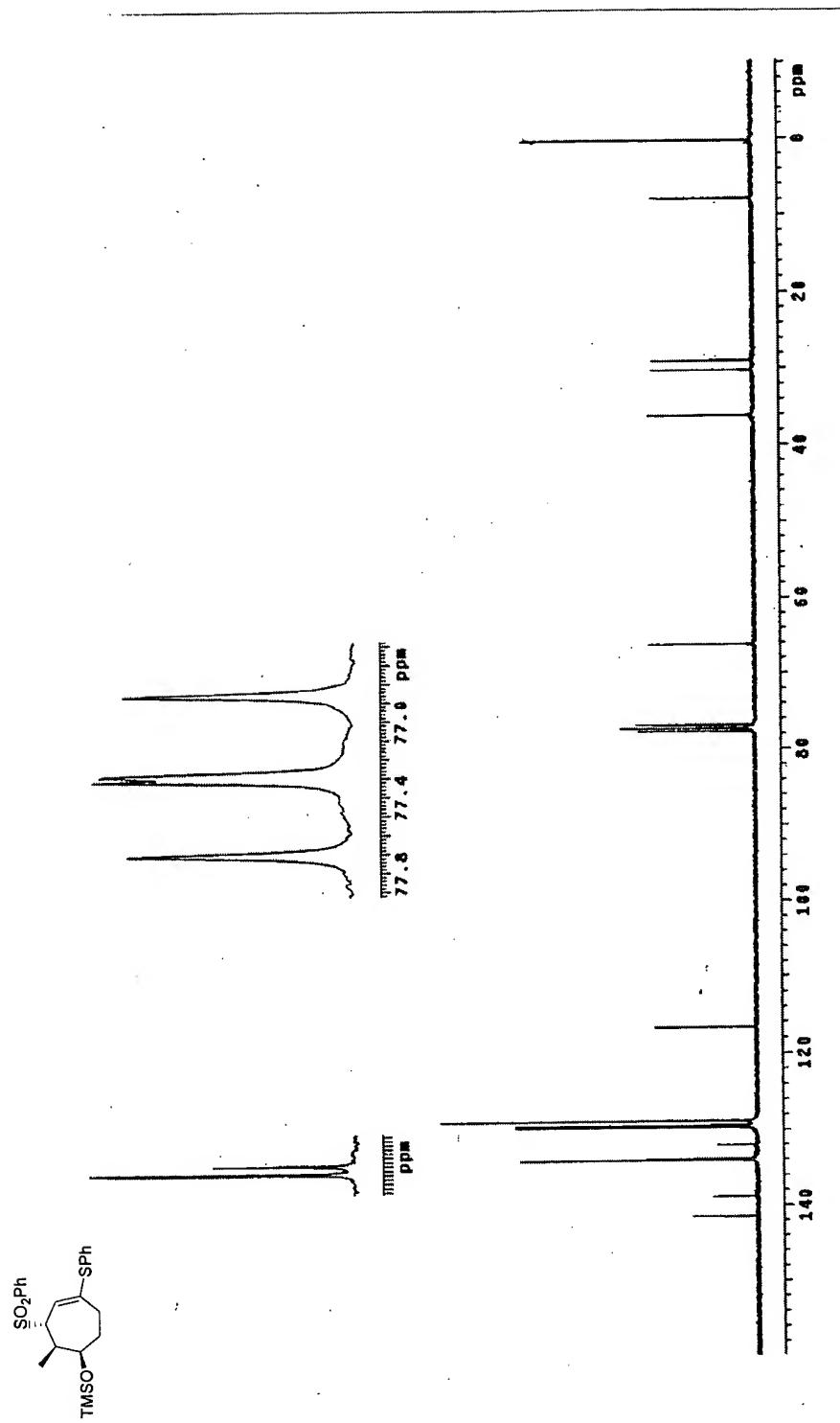


FIGURE 8 (Cont'd)



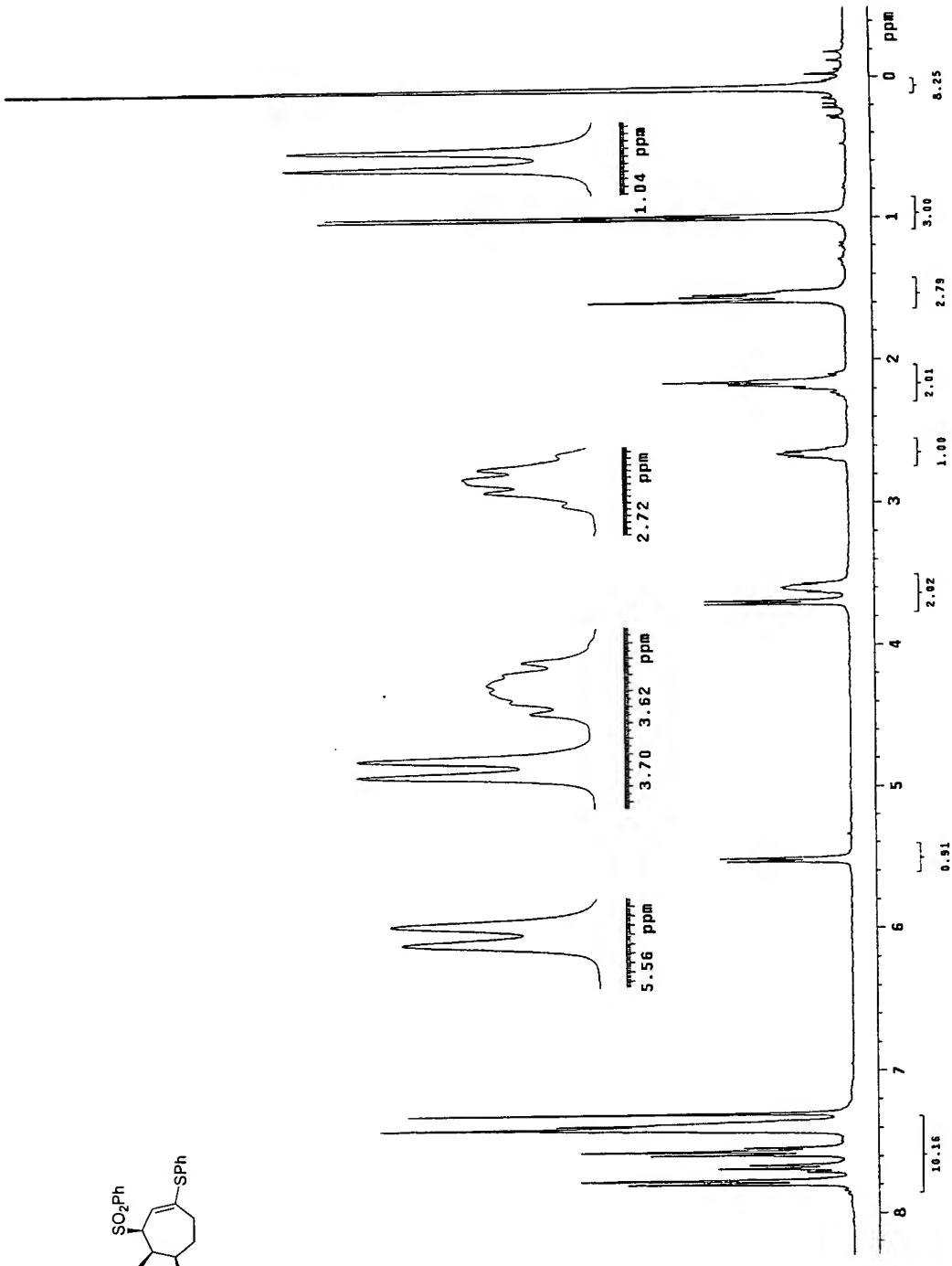
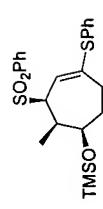
300MHz ^1H NMR of compound 23 α in CDCl₃

FIGURE 8 (Cont'd)



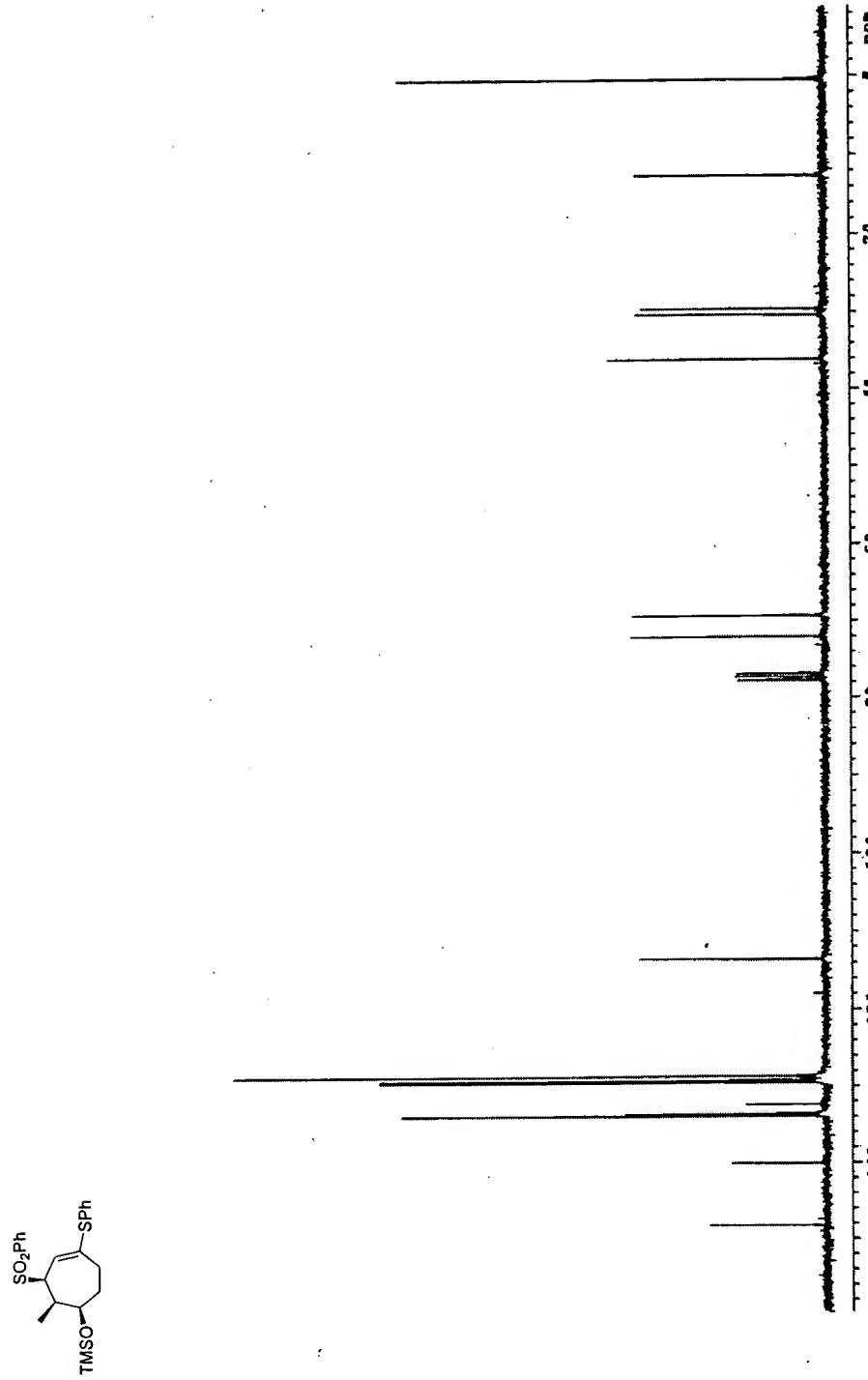
75MHz ^{13}C NMR of compound 23 α in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 23 β in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 23 β in CDCl_3

FIGURE 8 (Cont'd)

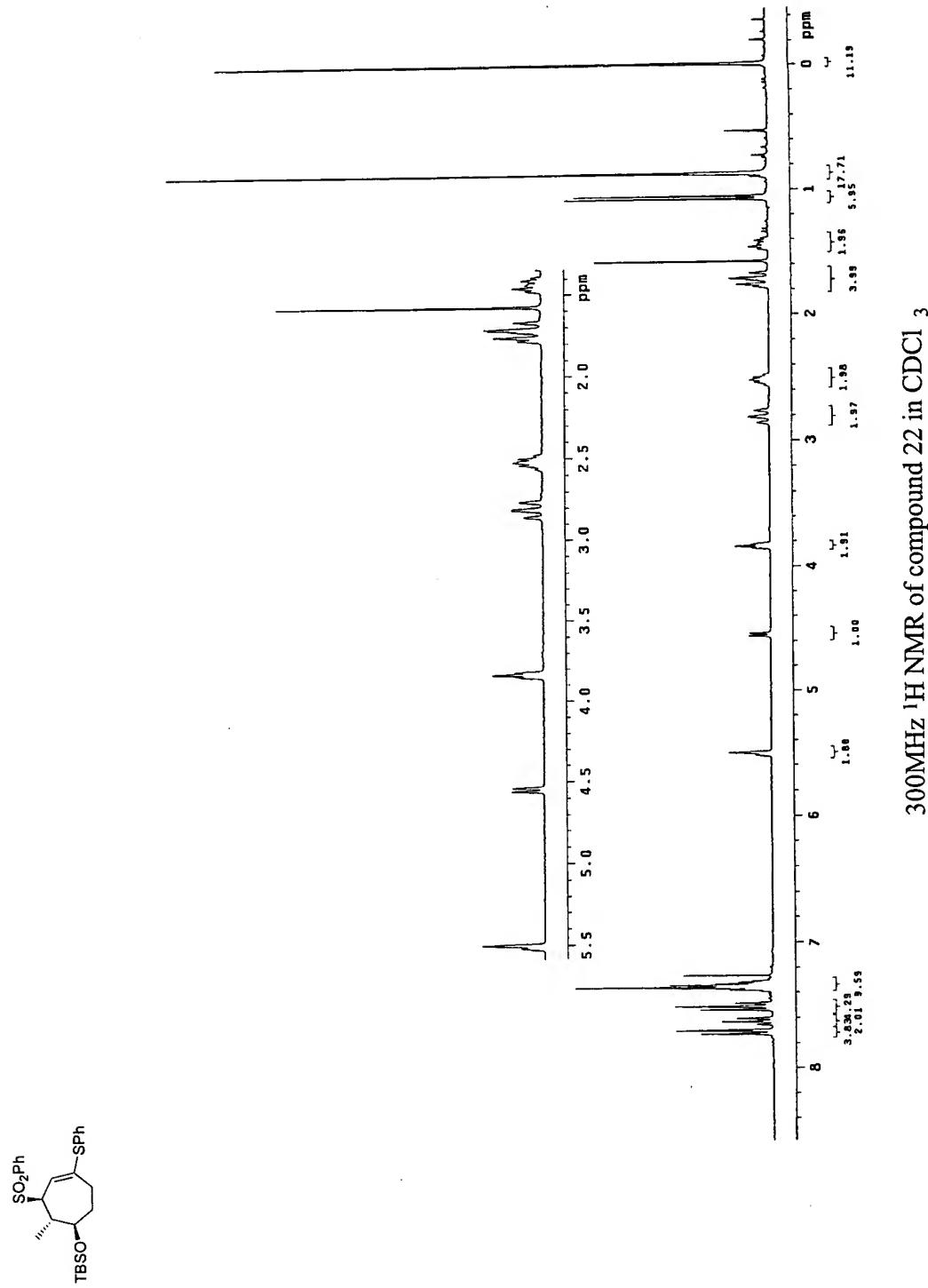


FIGURE 8 (Cont'd)

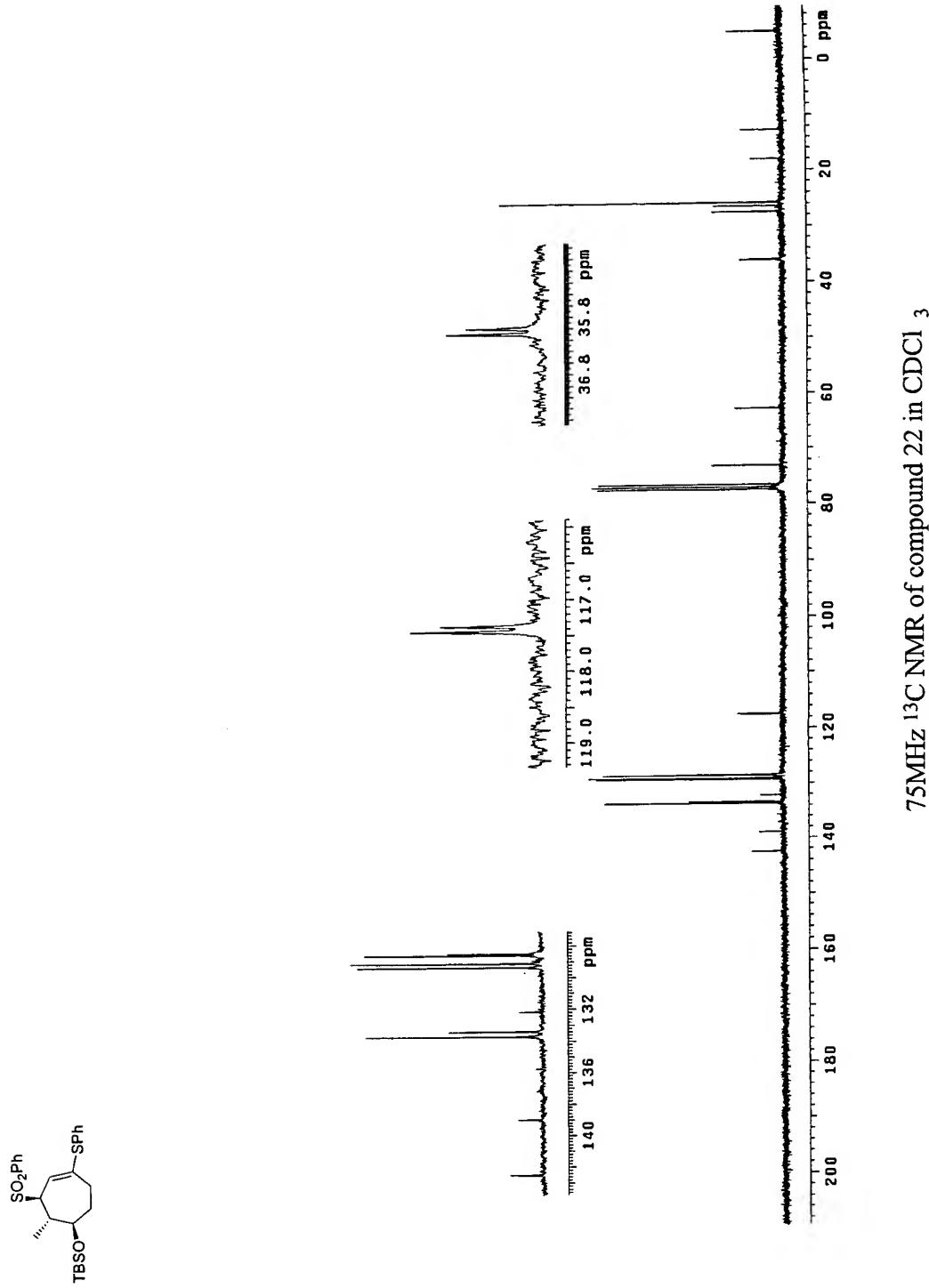


FIGURE 8 (Cont'd)

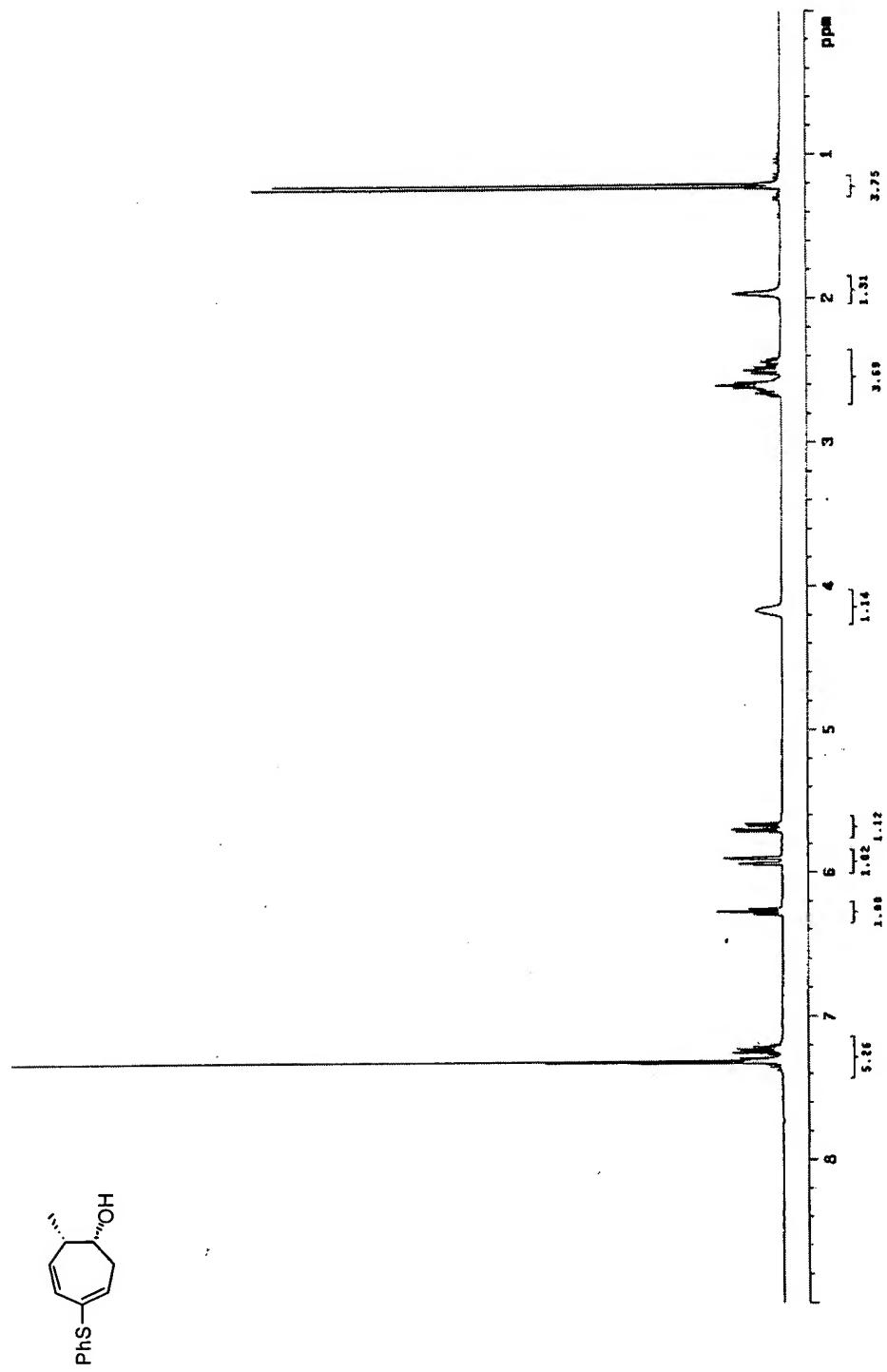


FIGURE 8 (Cont'd)

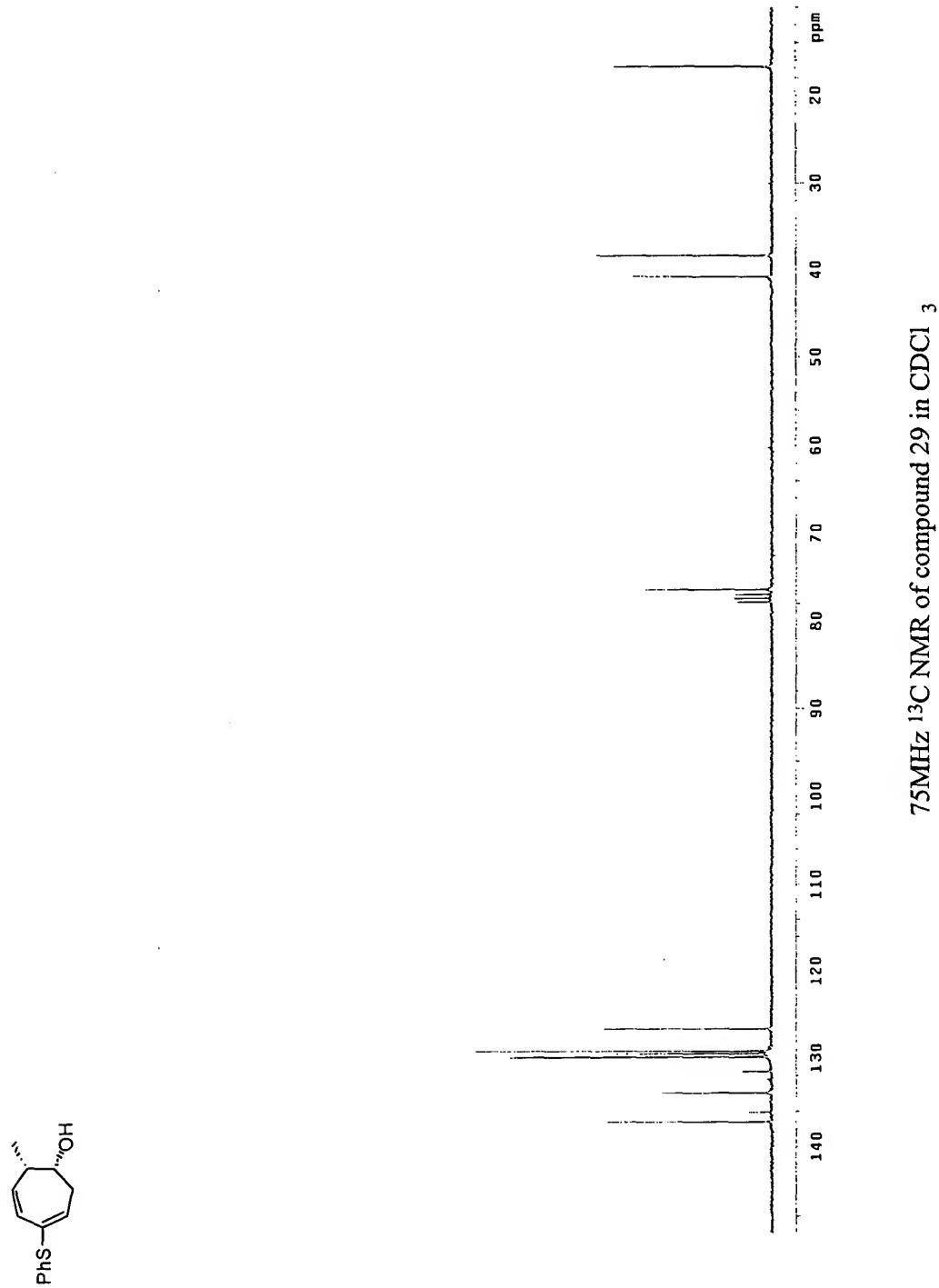
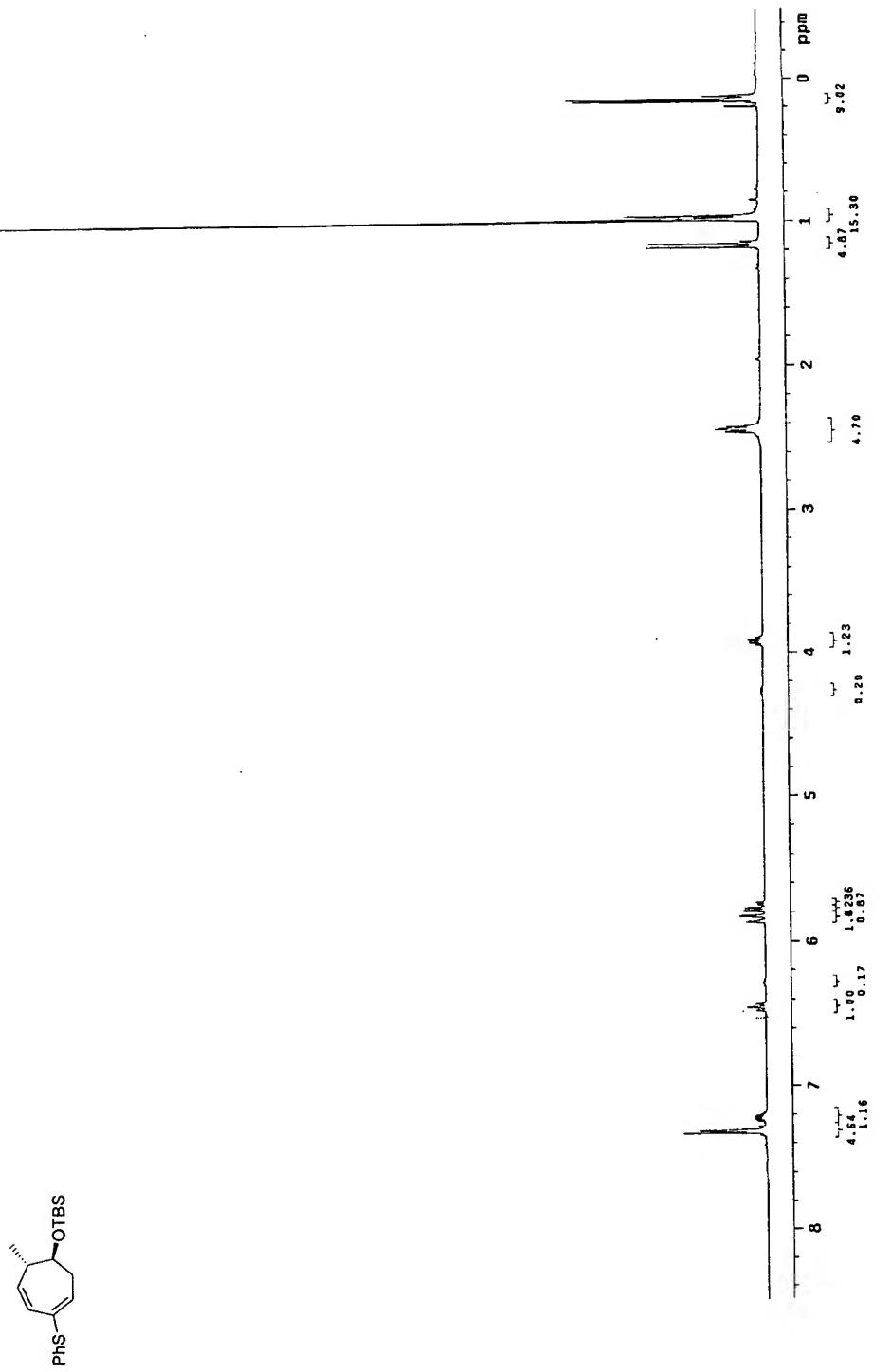
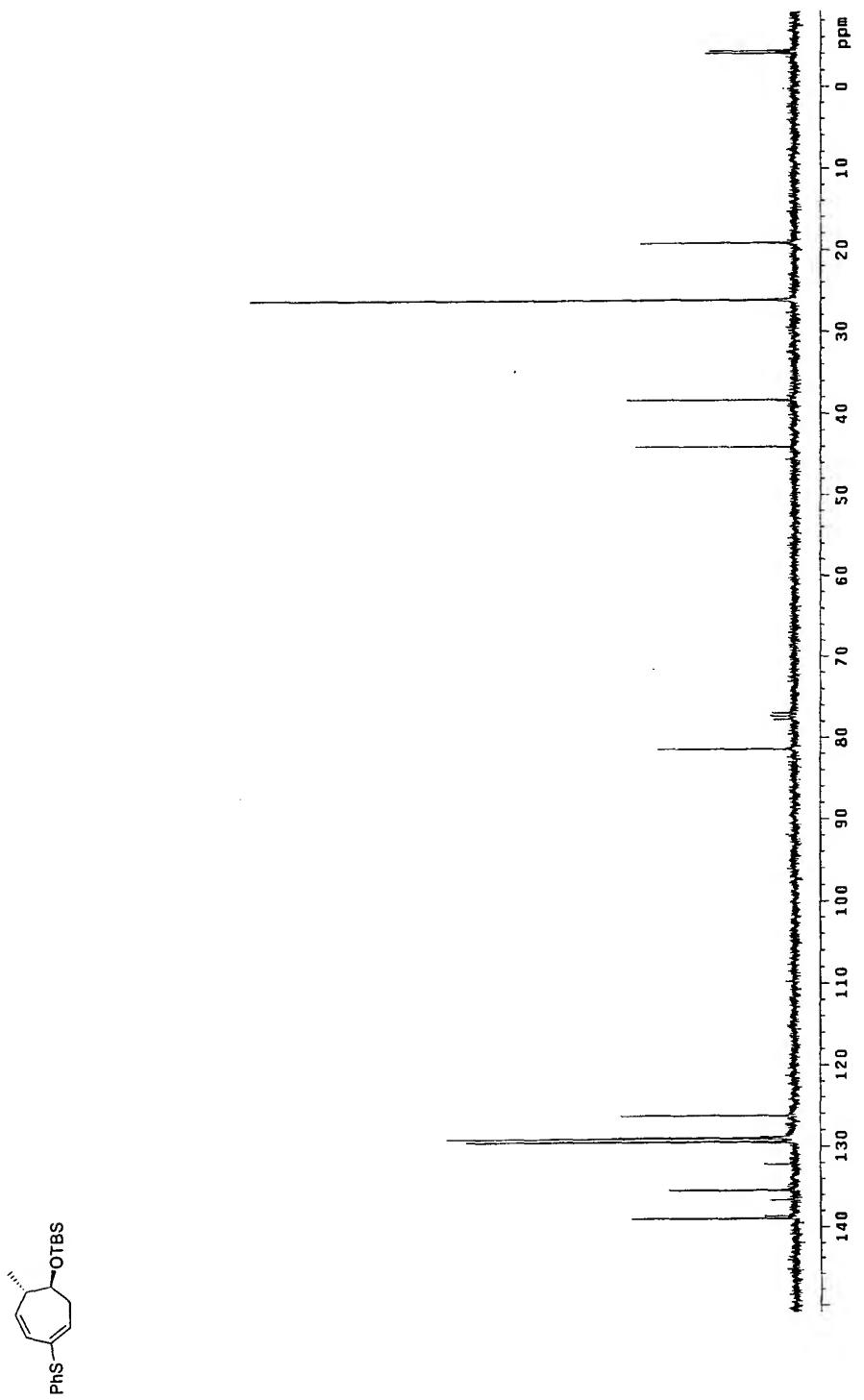


FIGURE 8 (Cont'd)



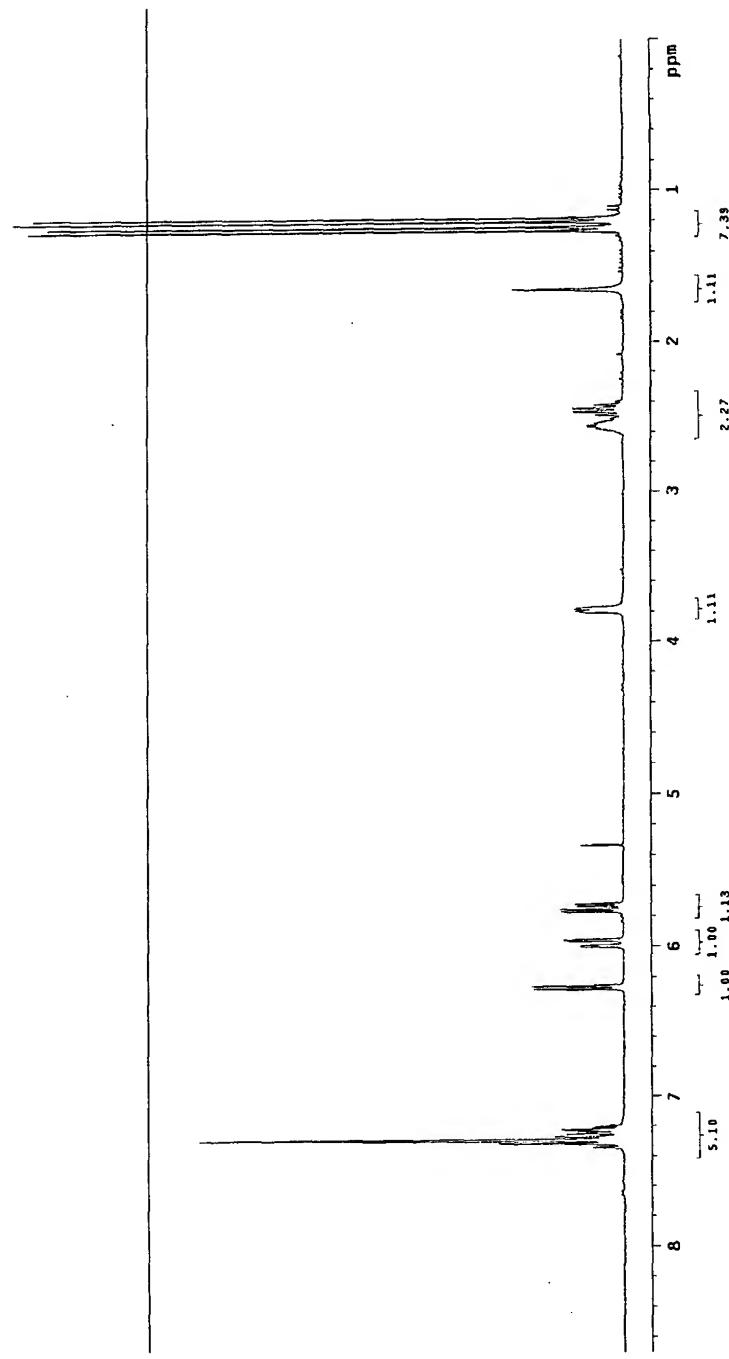
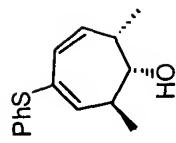
300MHz ^1H NMR of compound 27 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 27 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 31 in CDCl_3

FIGURE 8 (Cont'd)

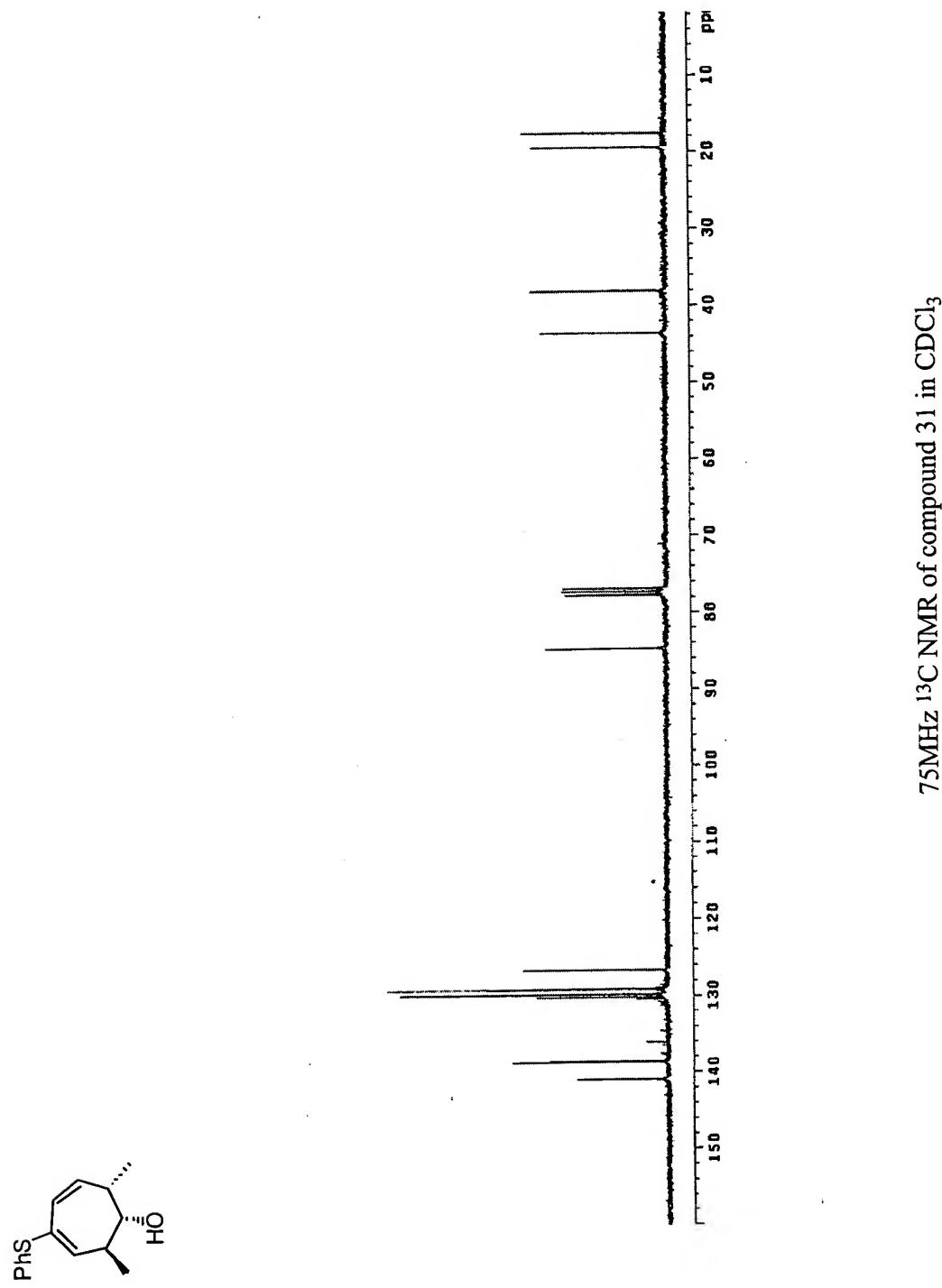
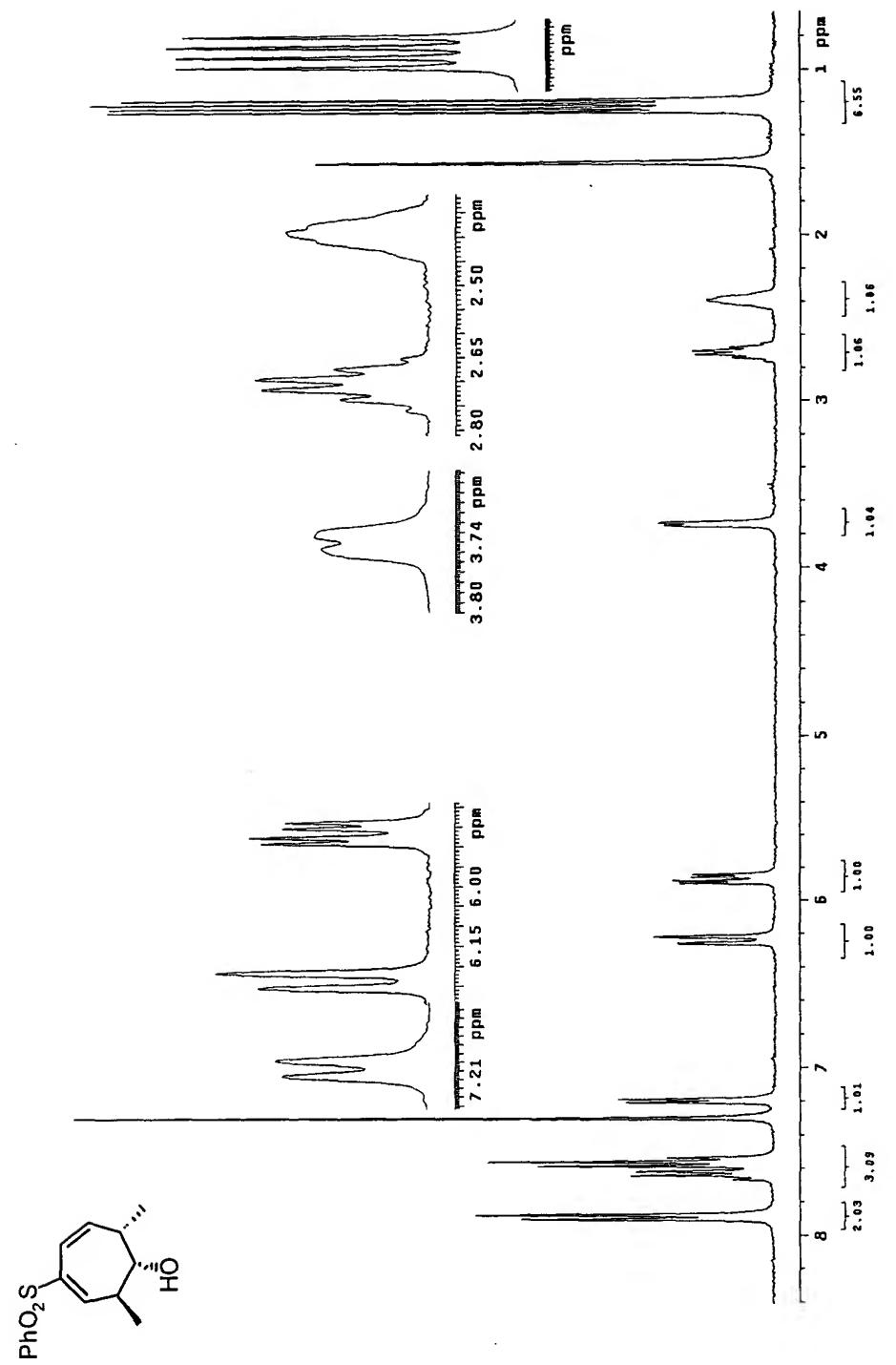


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 32 in CDCl_3

FIGURE 8 (Cont'd)

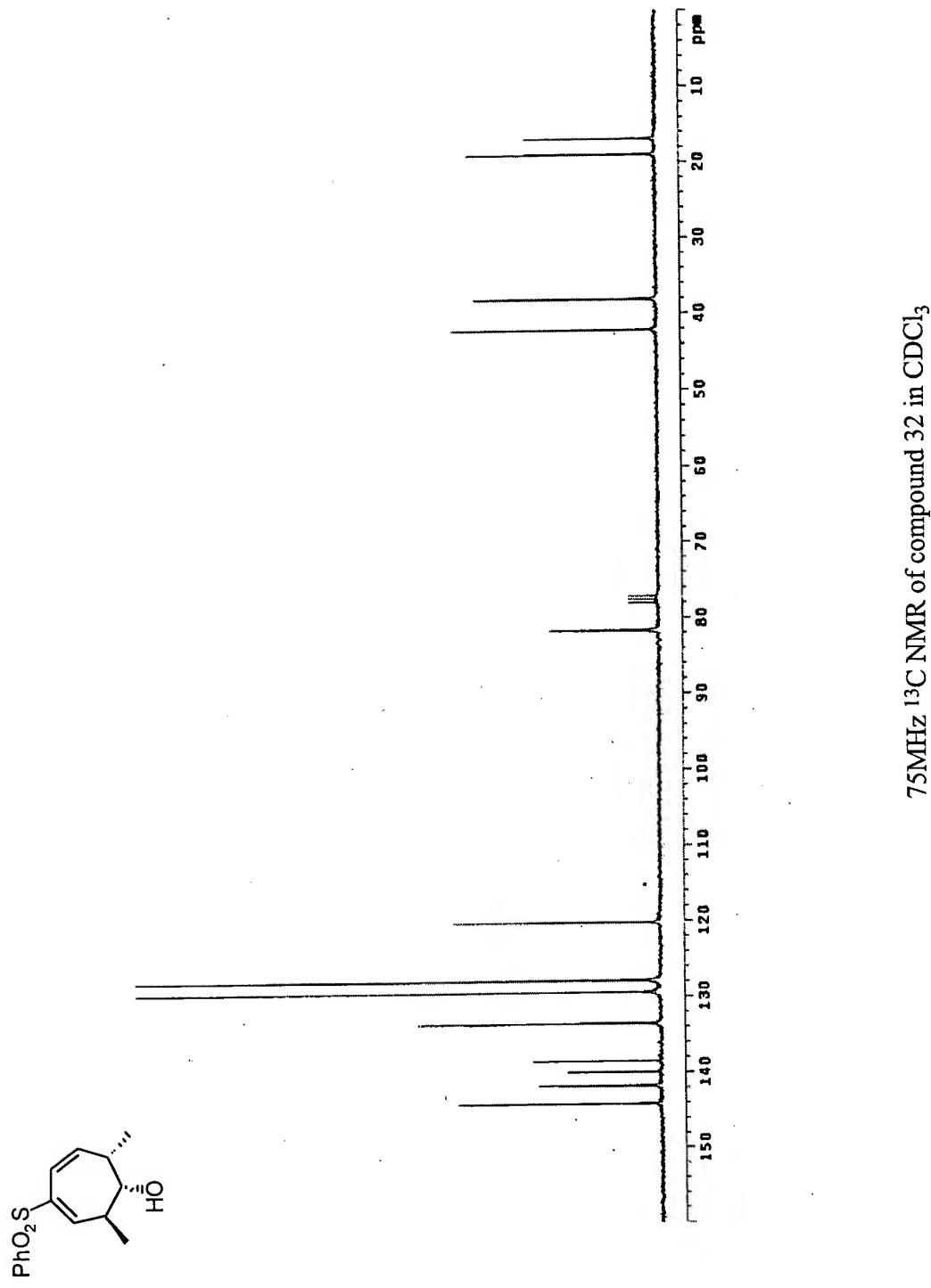


FIGURE 8 (Cont'd)

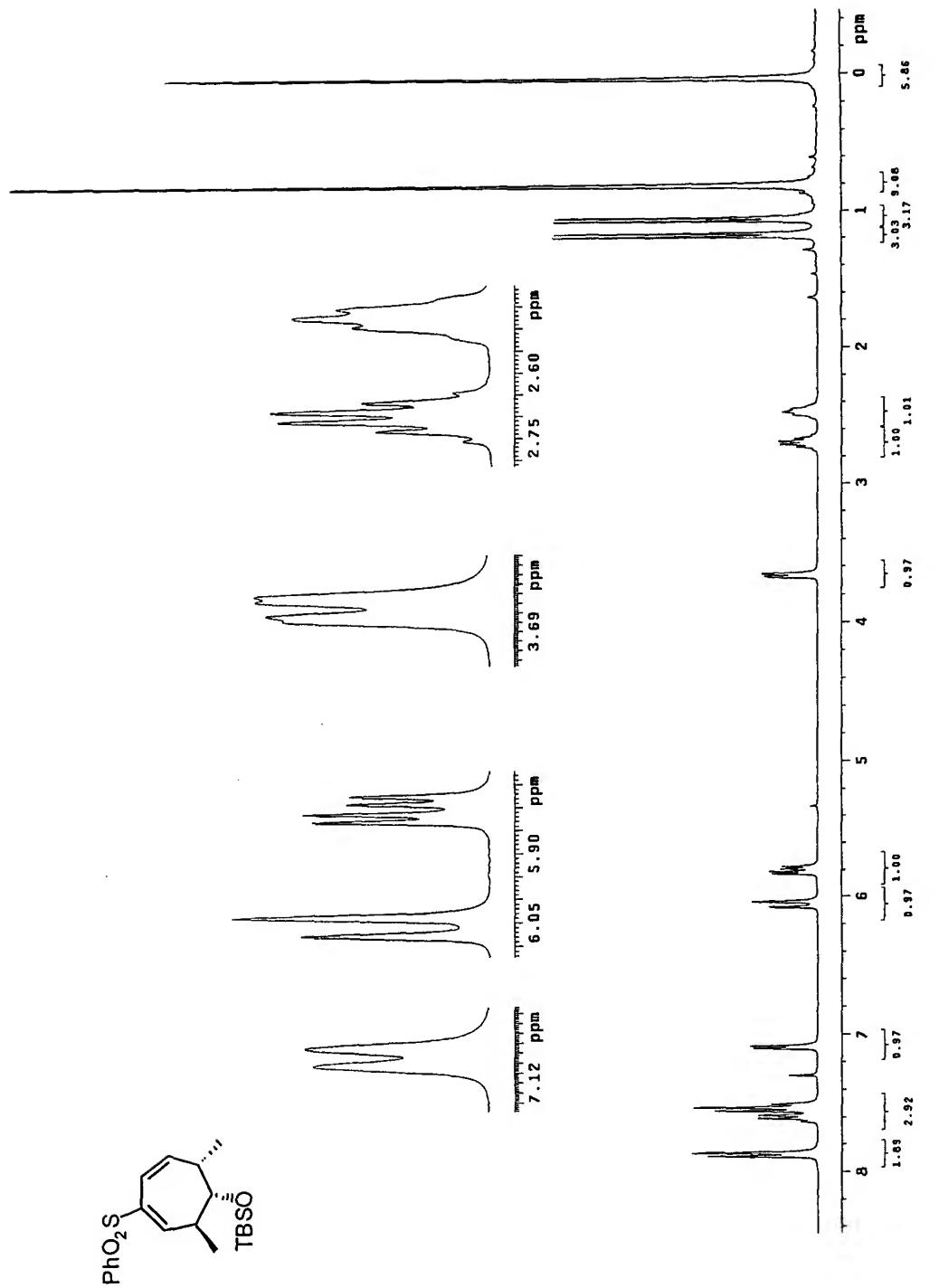
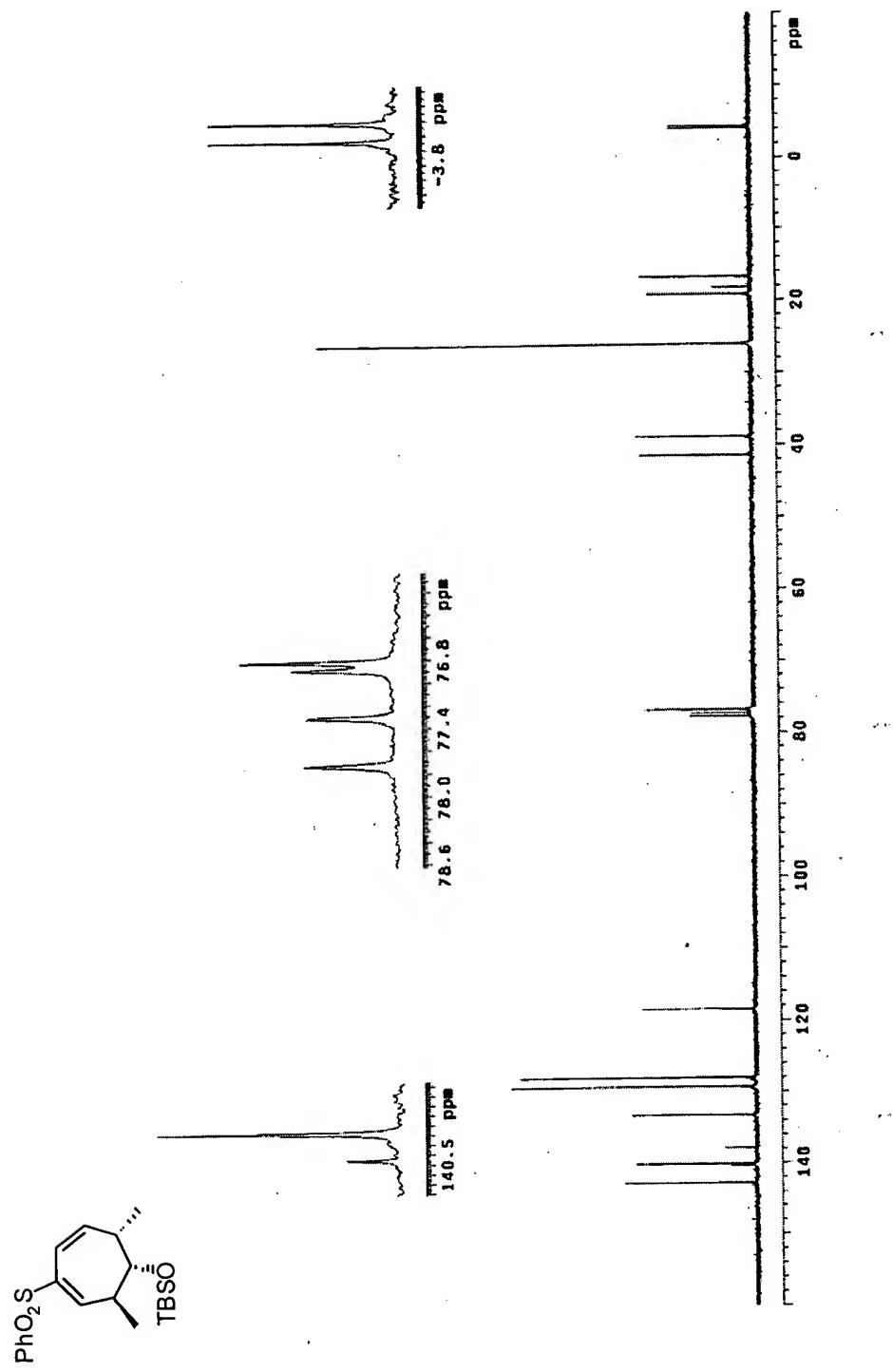
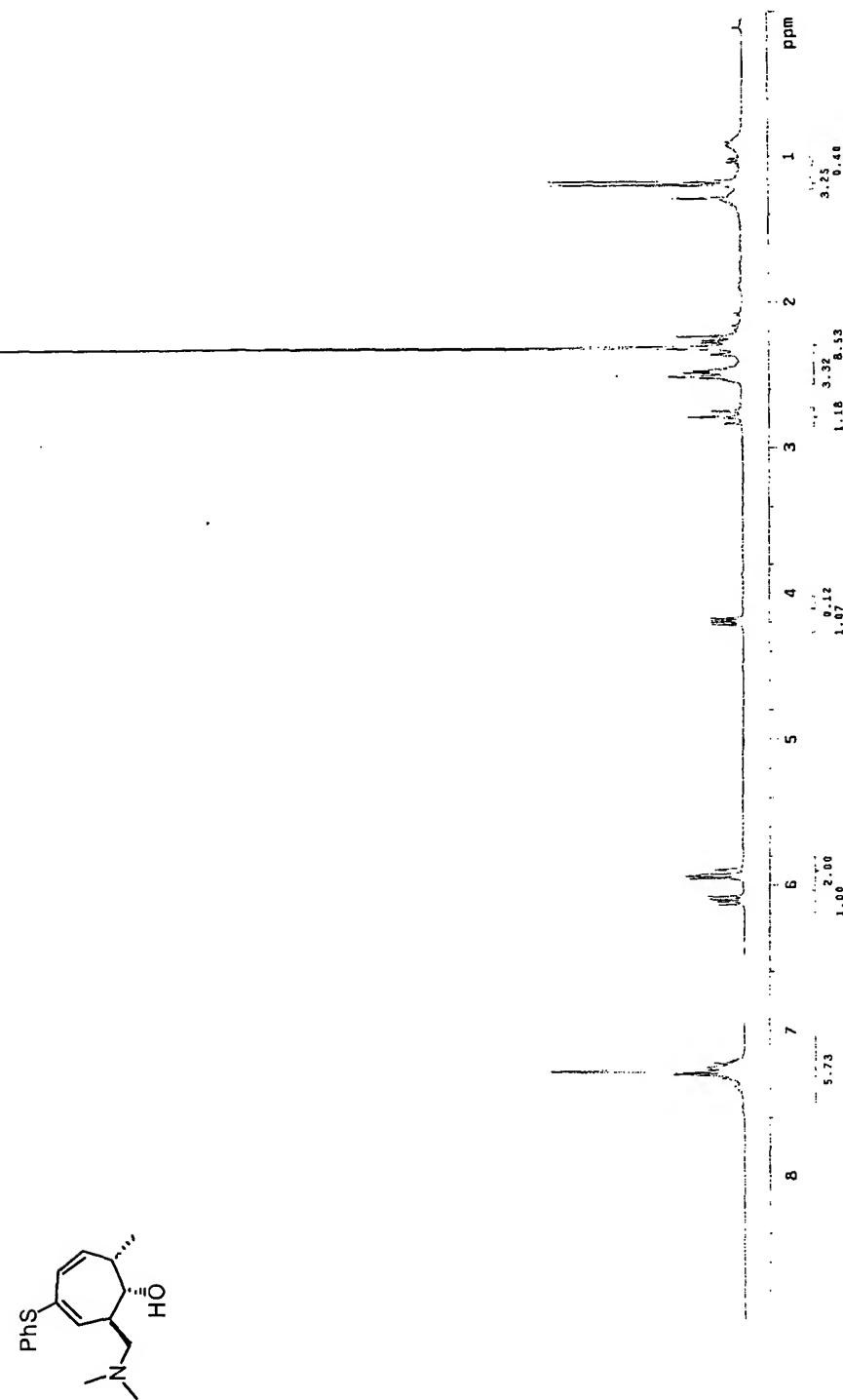


FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 33 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 34 in CDCl_3

FIGURE 8 (Cont'd)

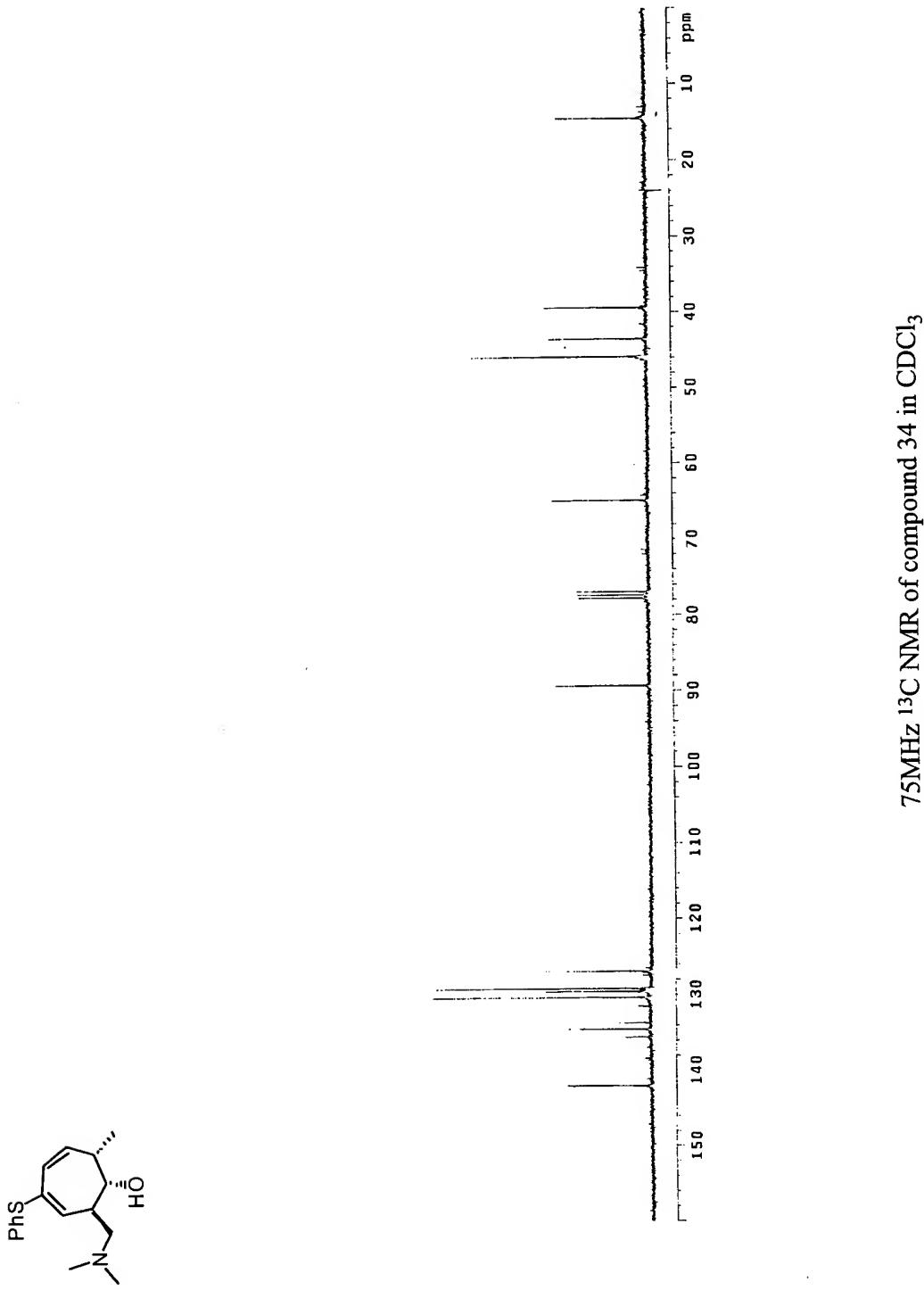
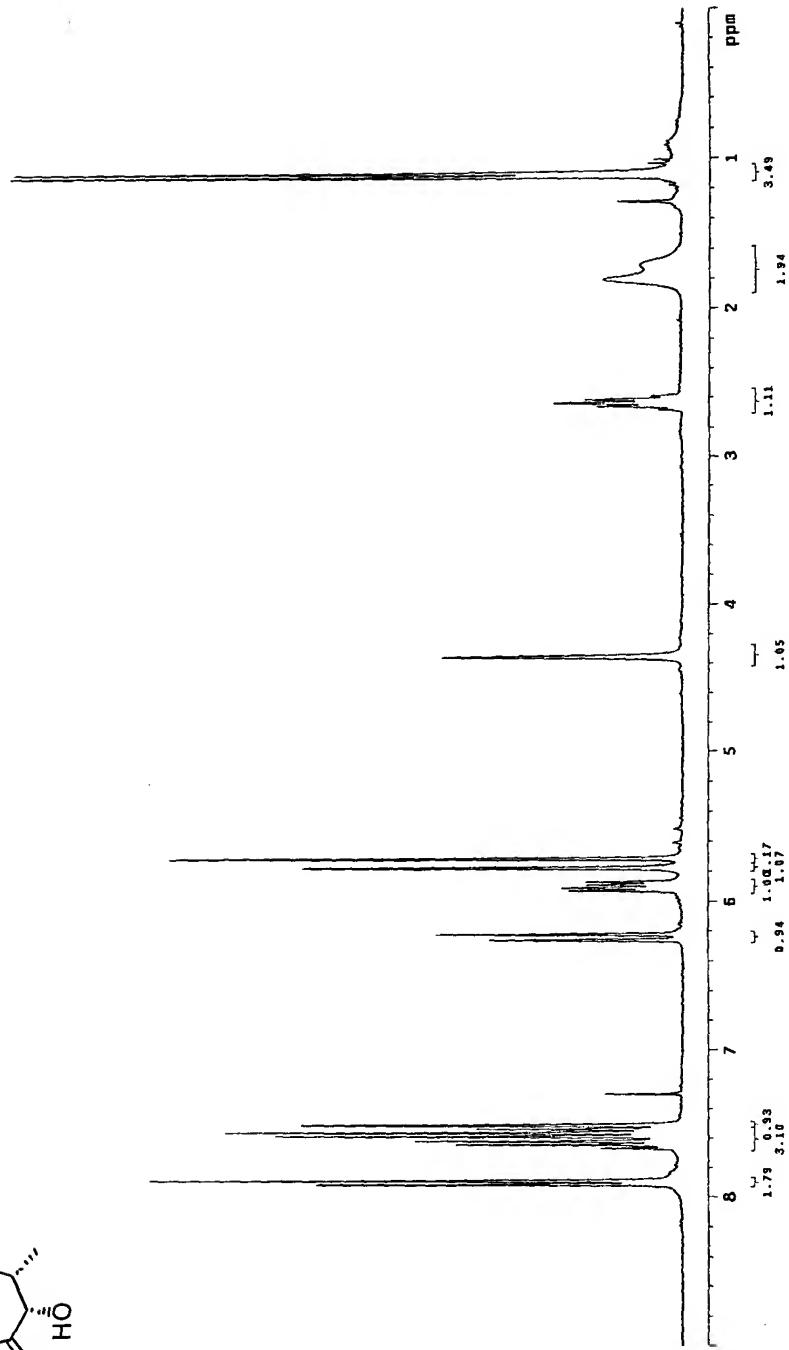
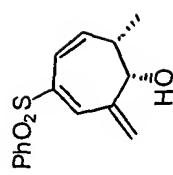


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 35 in CDCl_3

FIGURE 8 (Cont'd)

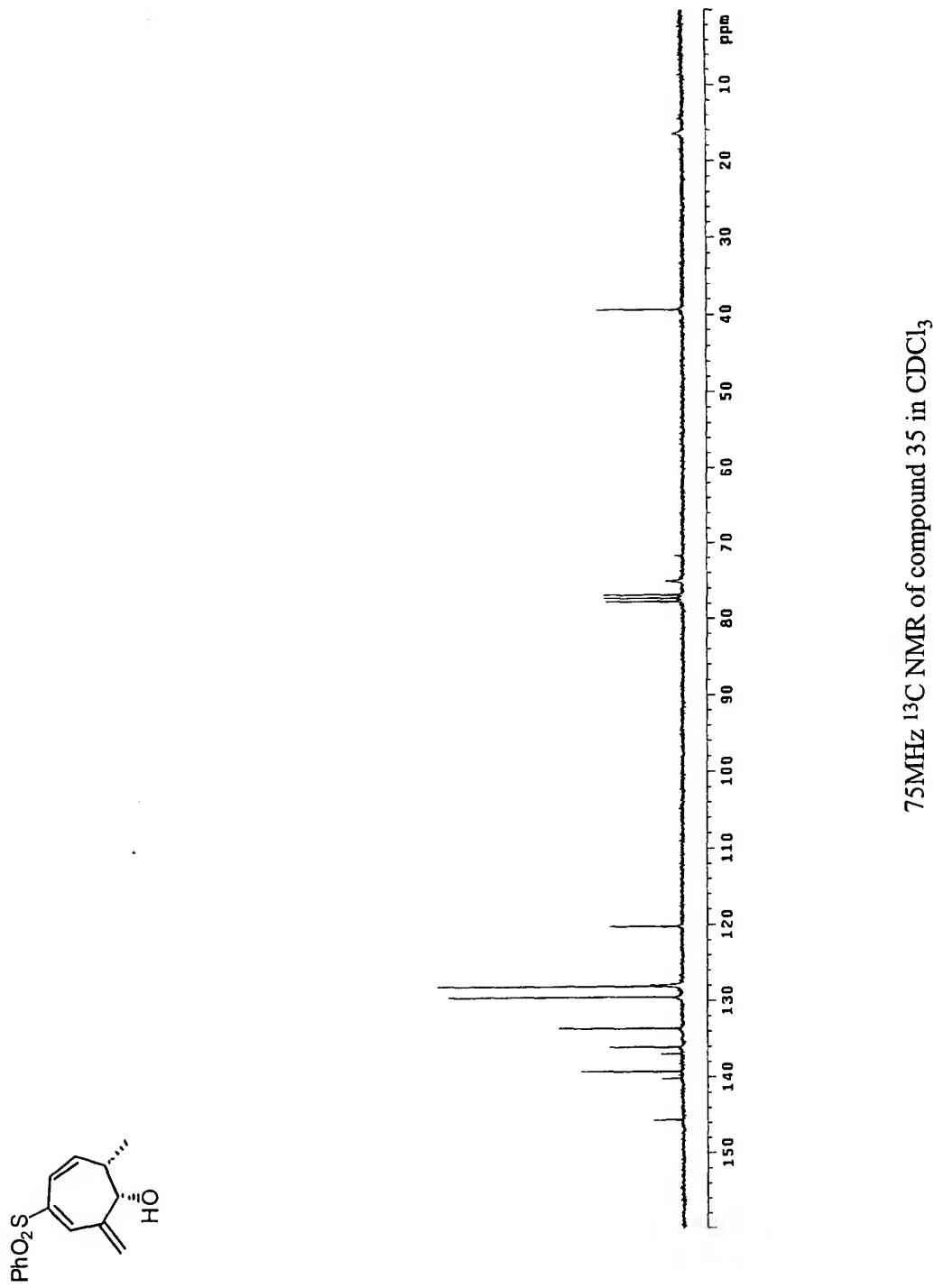
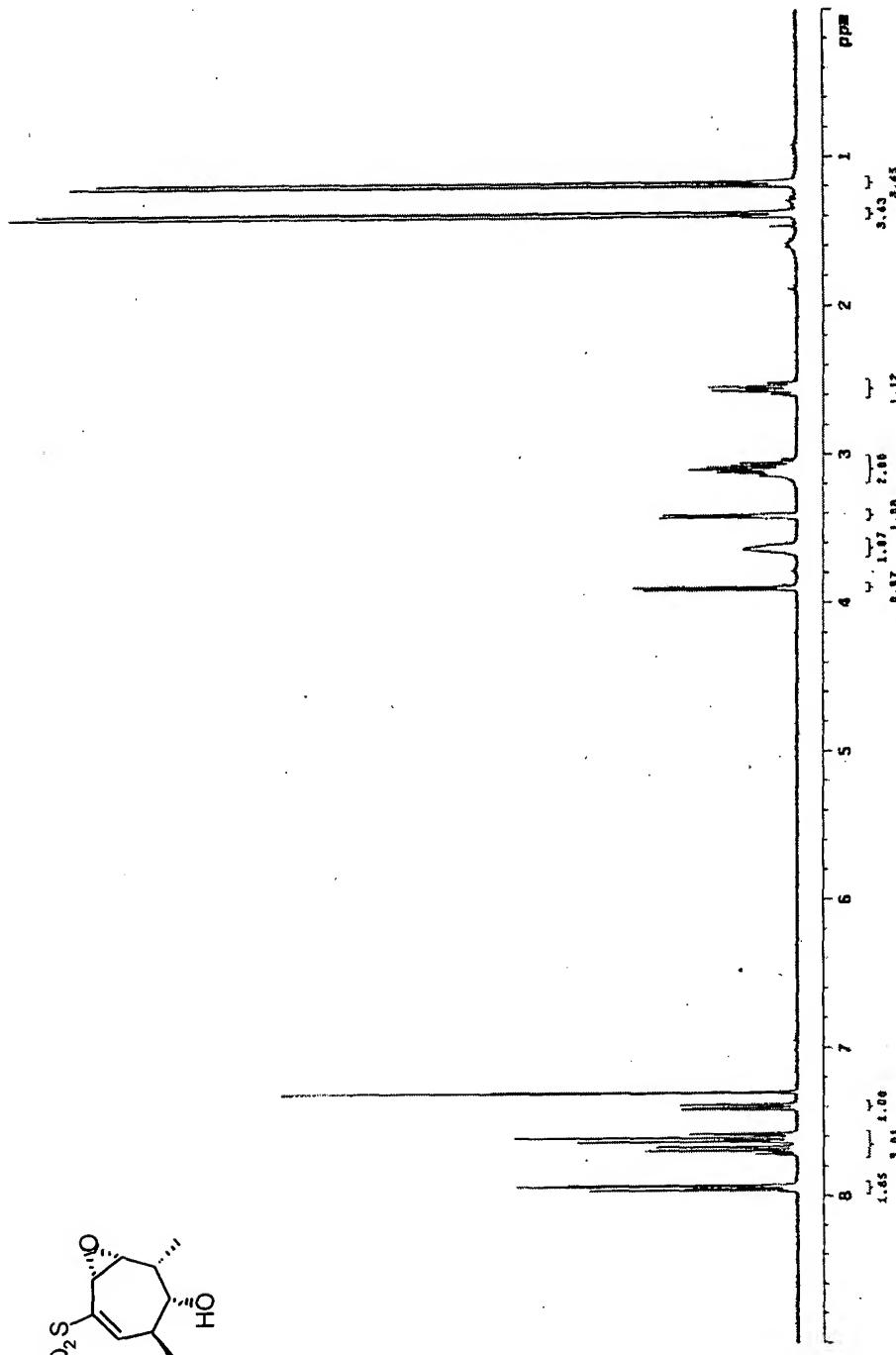
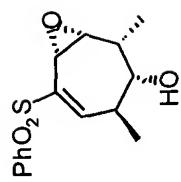
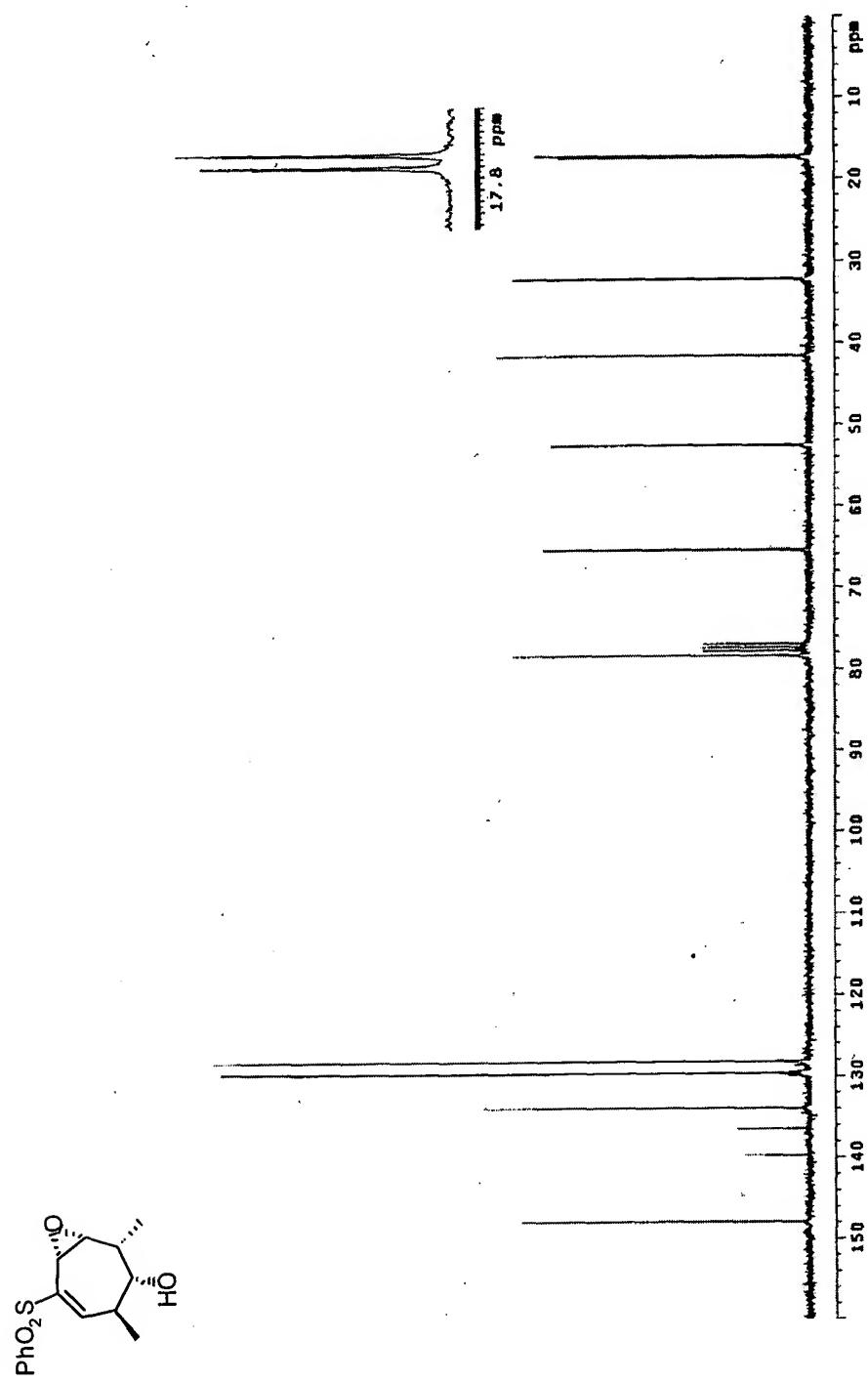


FIGURE 8 (Cont'd)



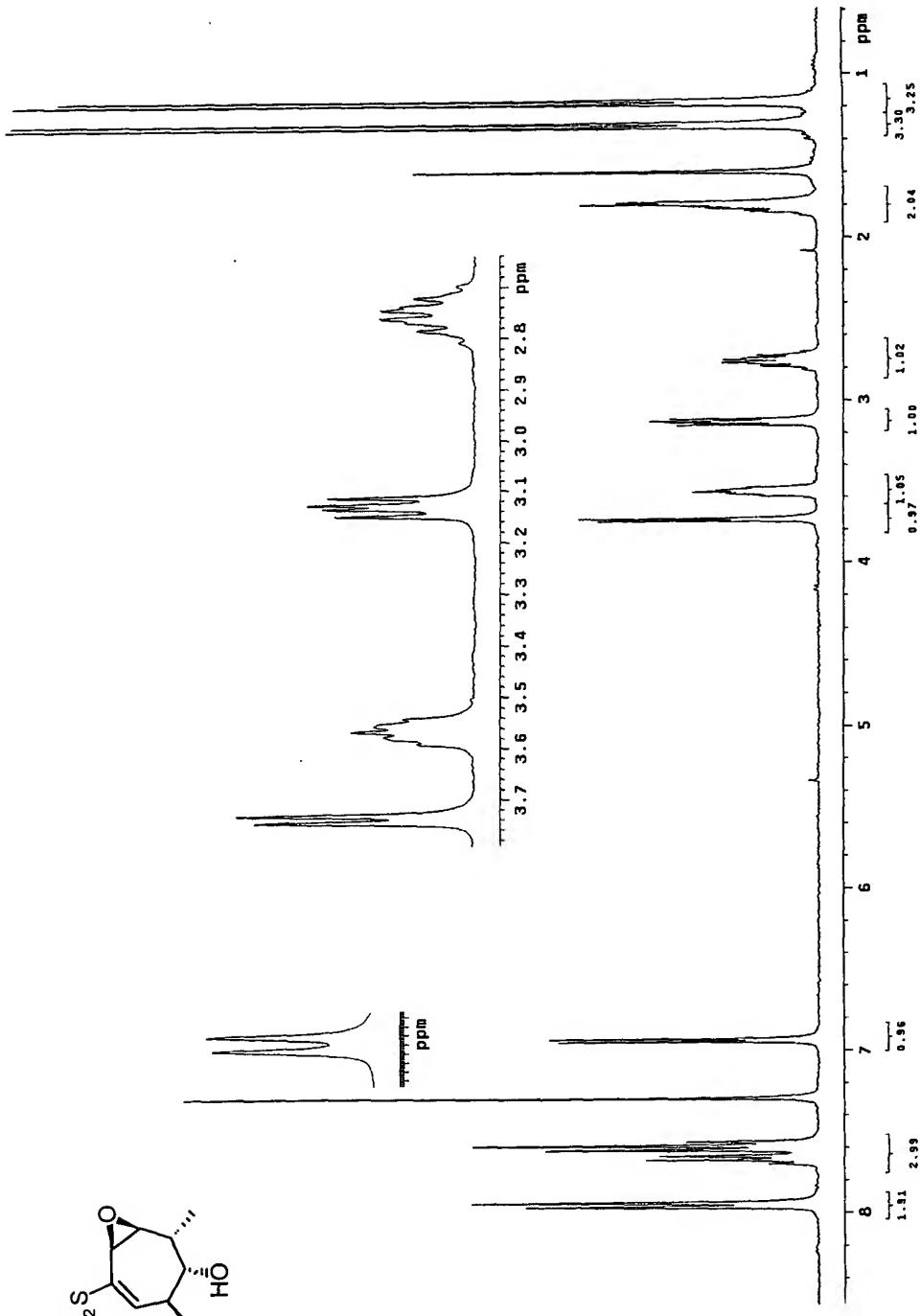
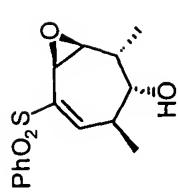
300MHz ^1H NMR of compound α 36 in CDCl_3

FIGURE 8 (Cont'd)



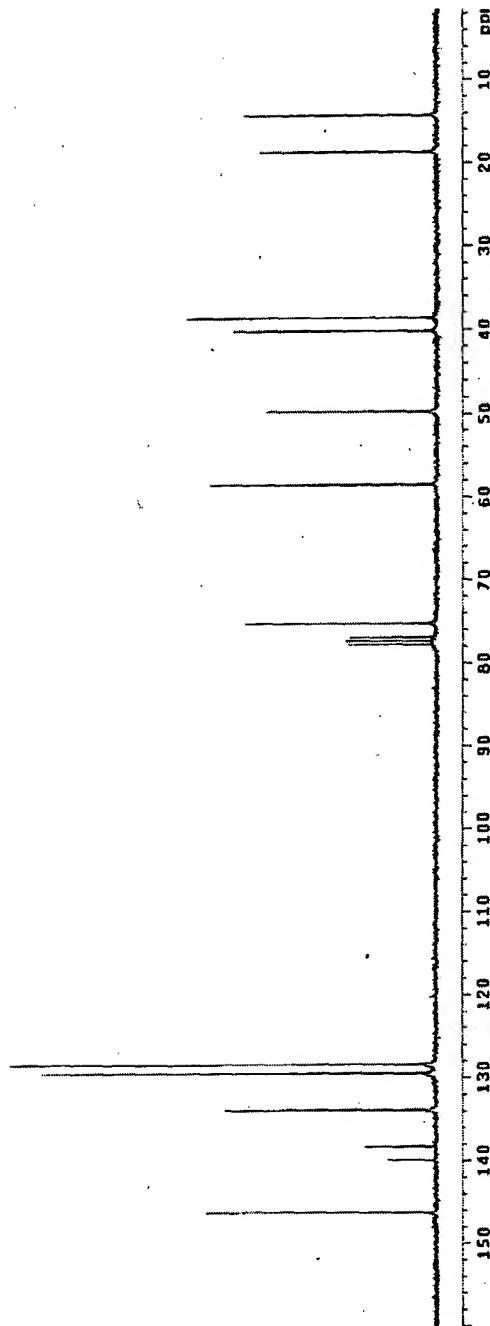
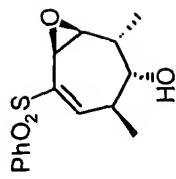
75MHz ^{13}C NMR of compound α 36 in CDCl_3

FIGURE 8 (Cont'd)



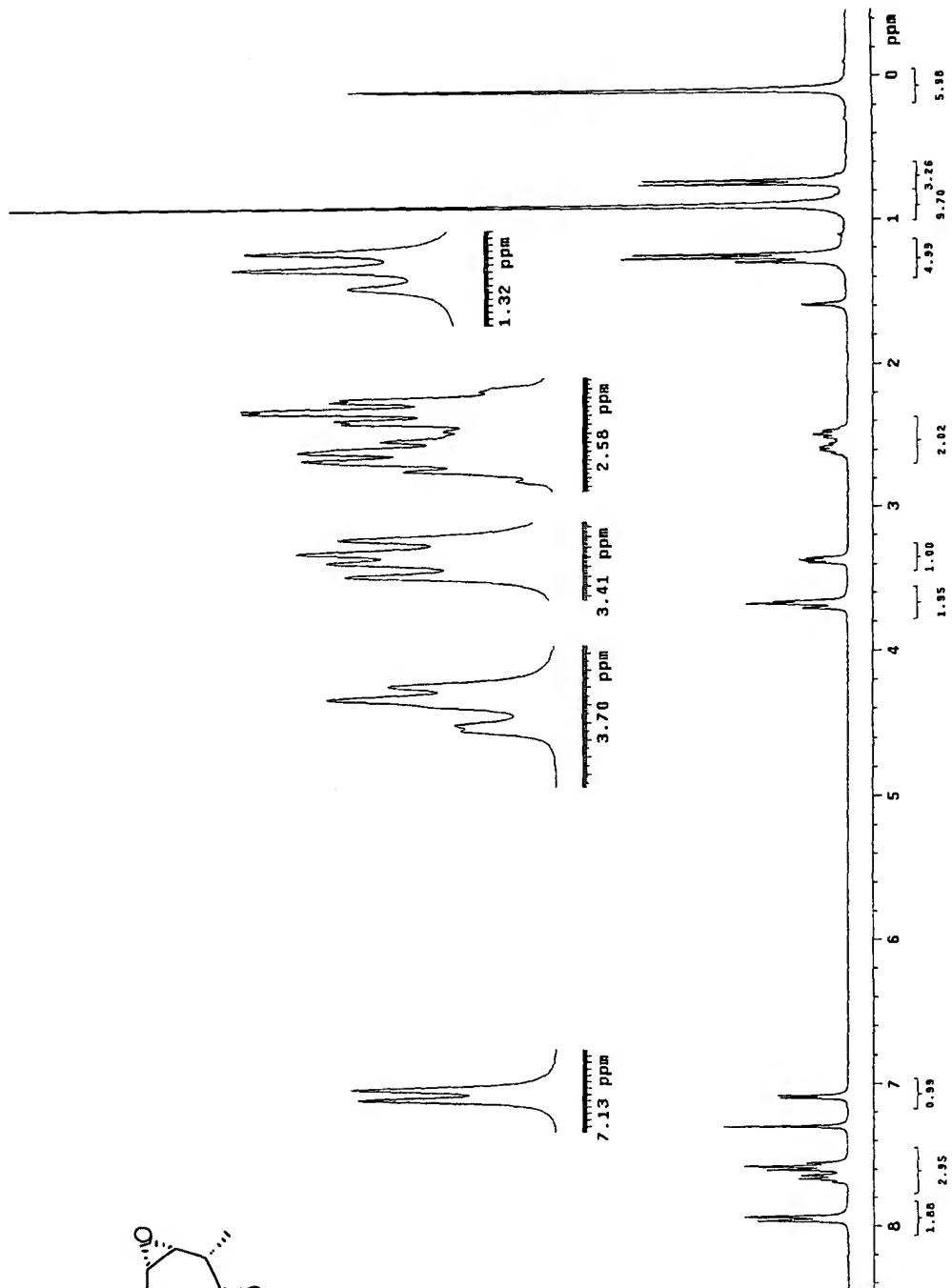
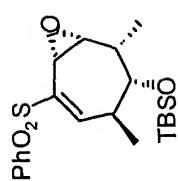
300MHz ^1H NMR of compound β 36 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound β 36 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound α 37 in CDCl_3

FIGURE 8 (Cont'd)

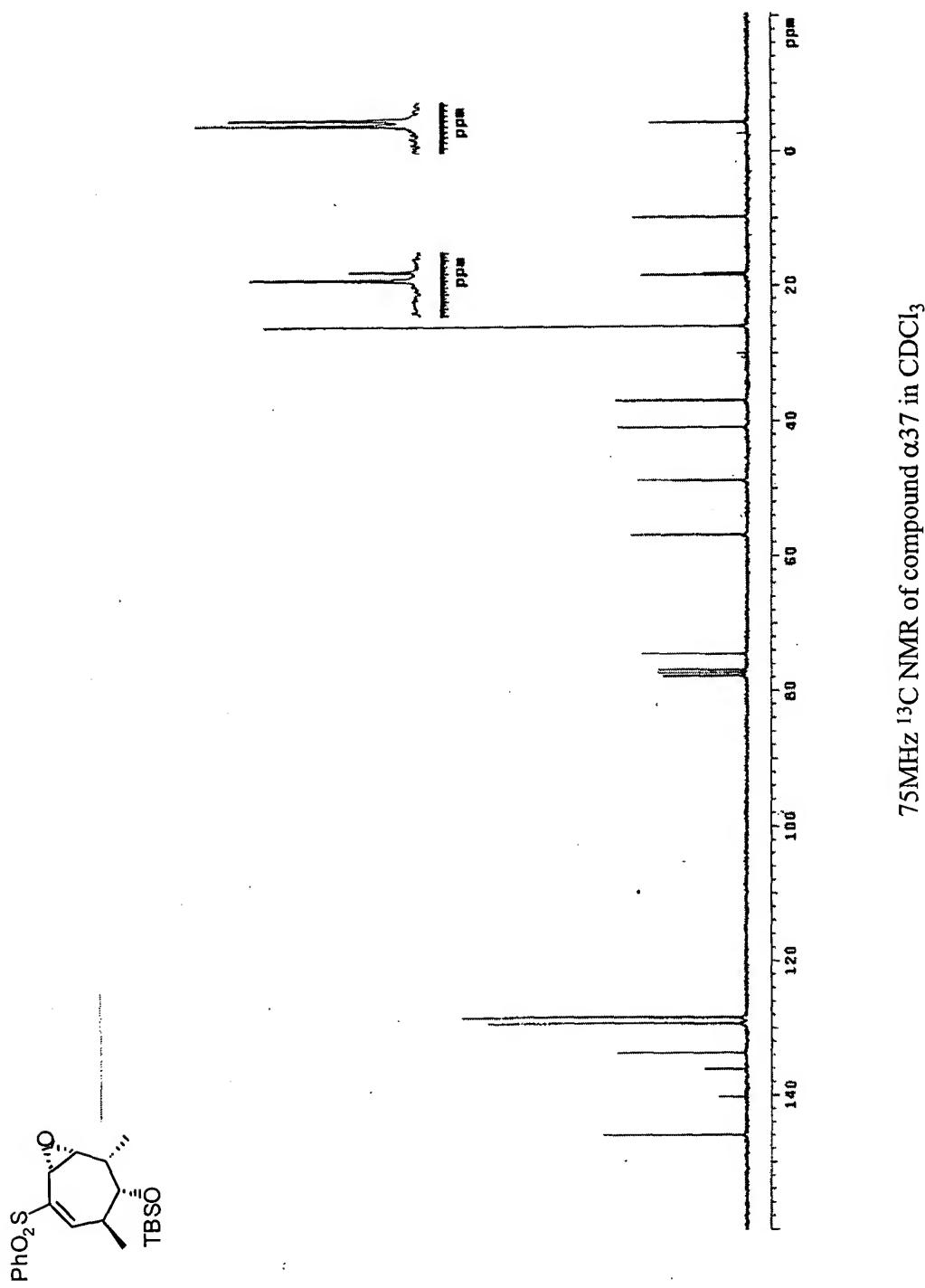
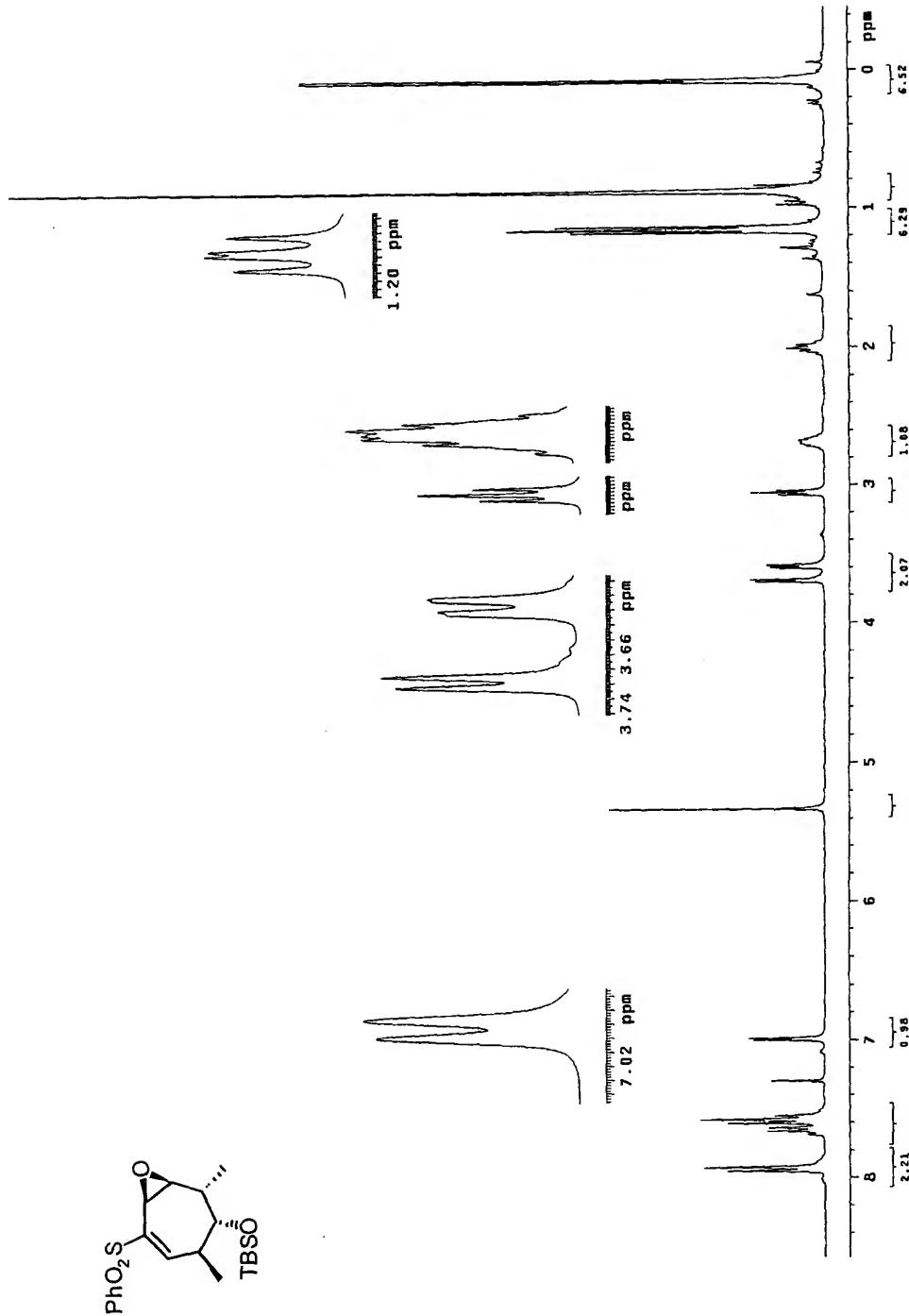
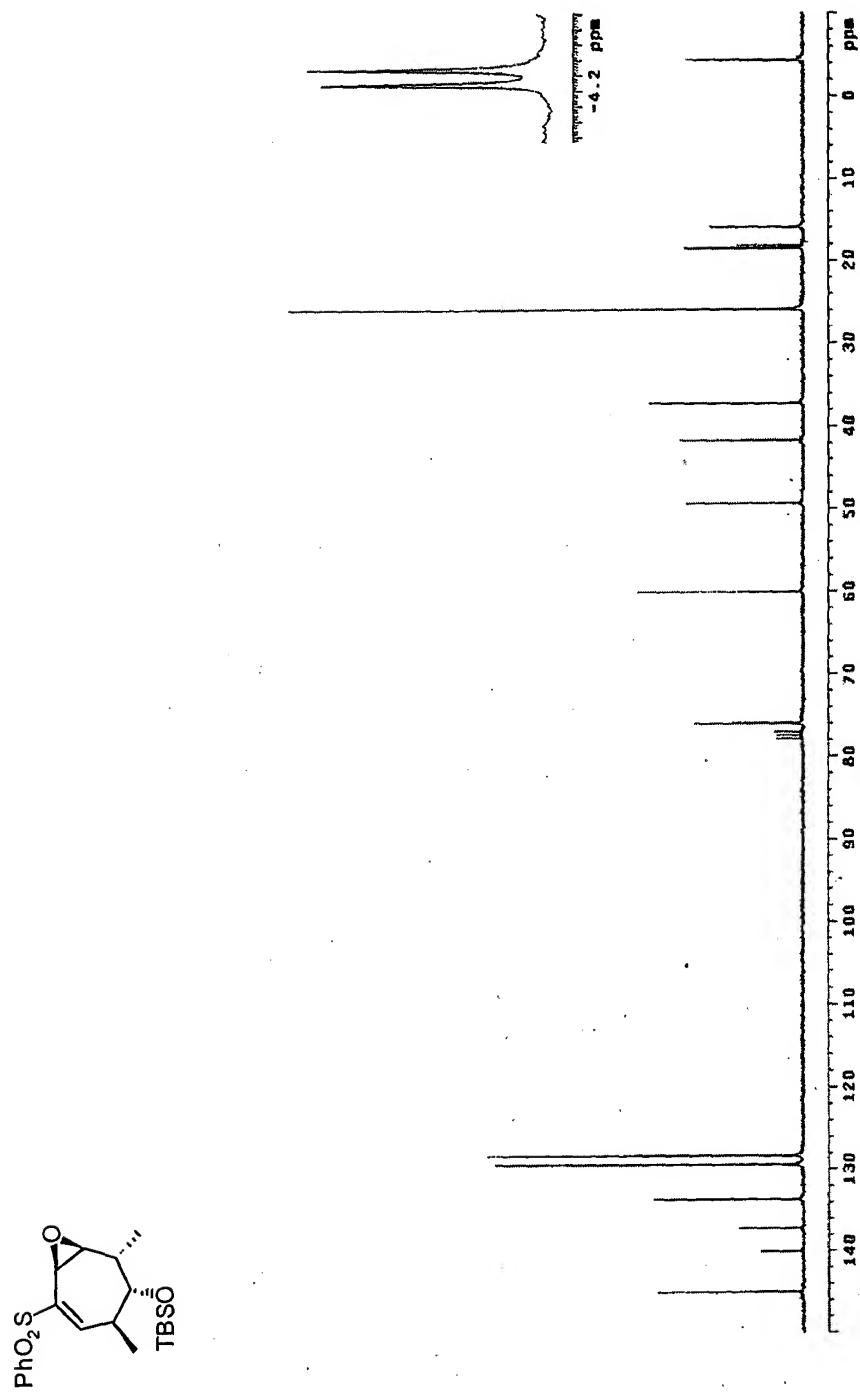


FIGURE 8 (Cont'd)



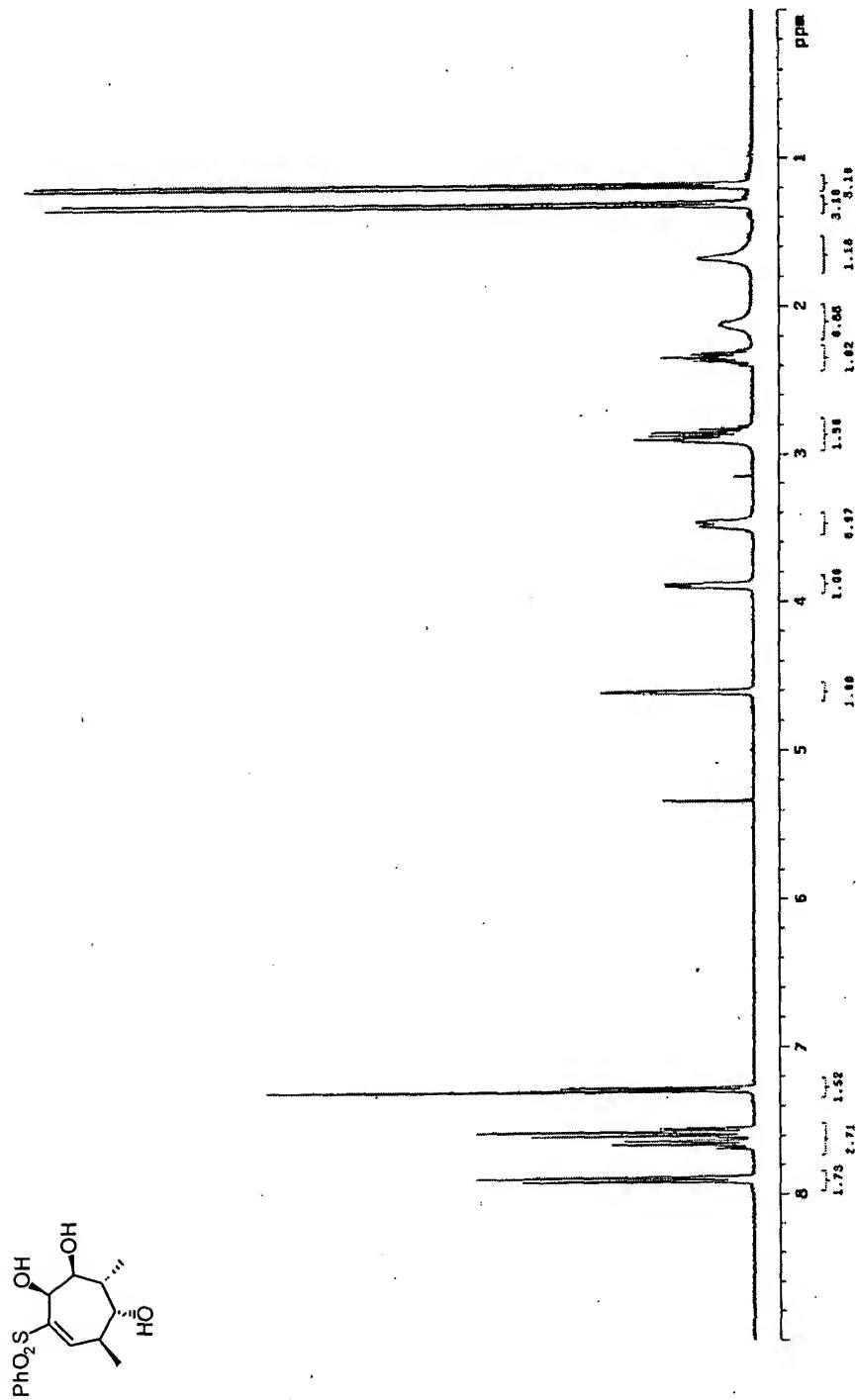
300MHz ^1H NMR of compound β 37 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound B37 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 38 in CDCl_3

FIGURE 8 (Cont'd)

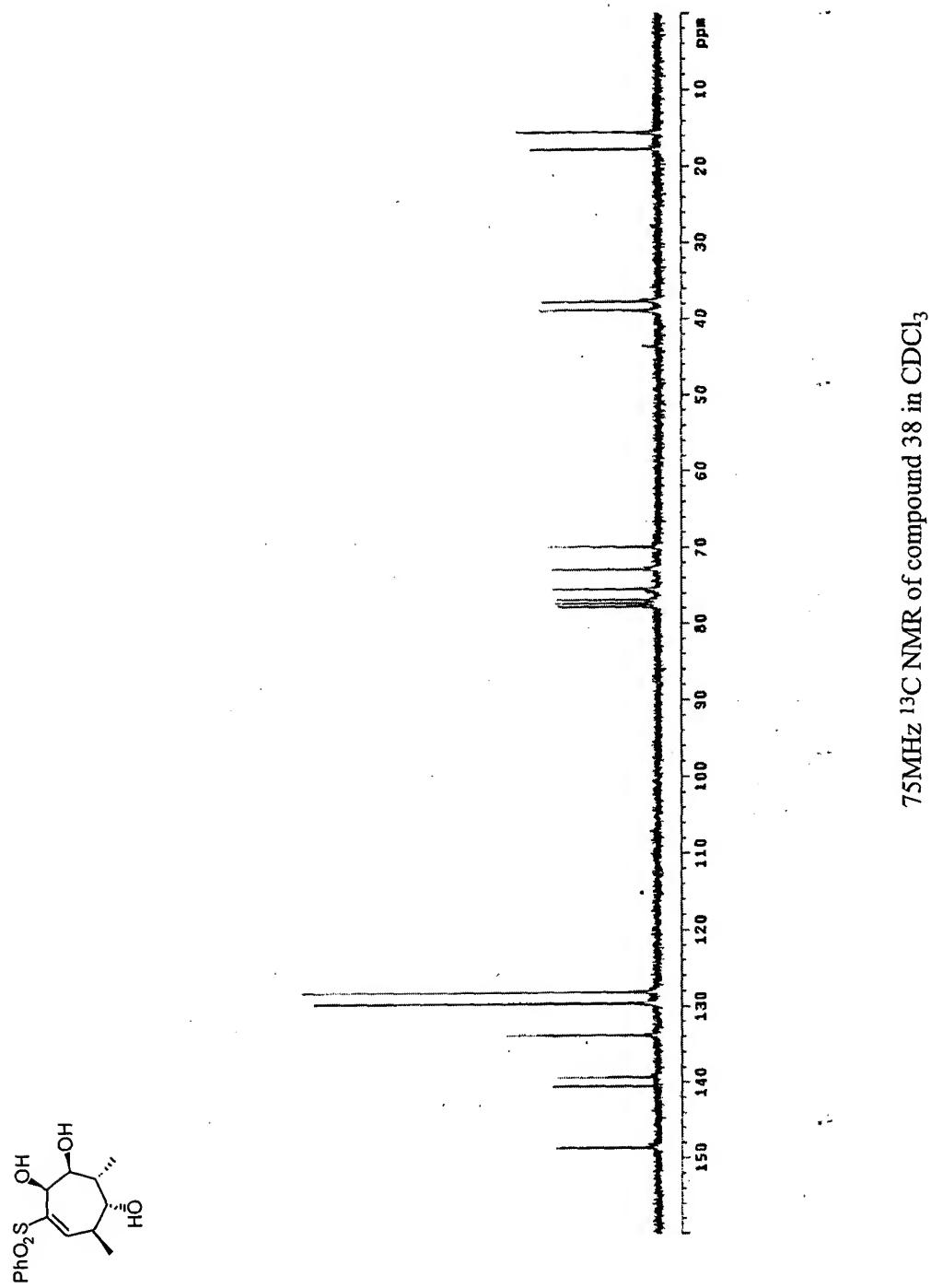


FIGURE 8 (Cont'd)

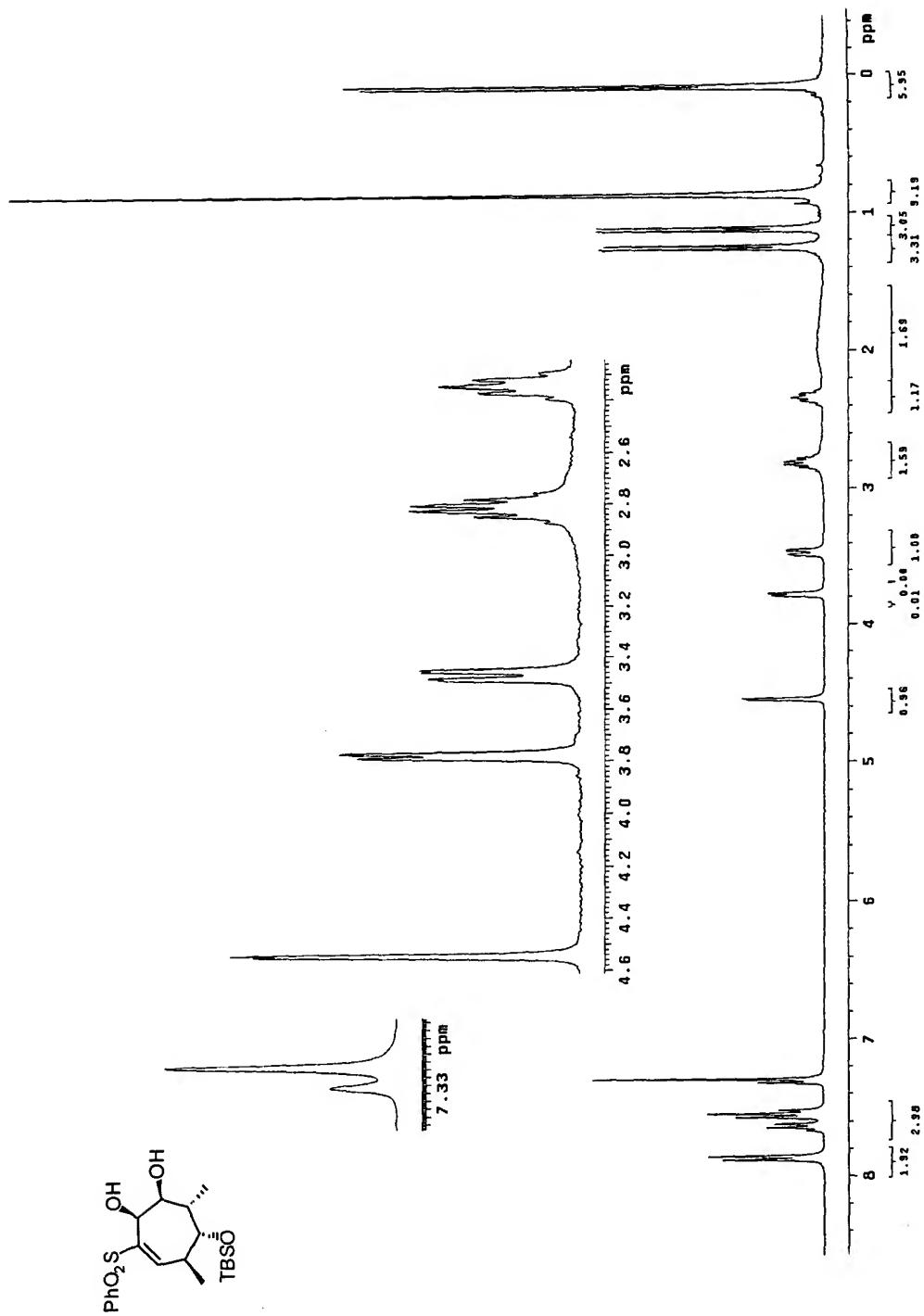
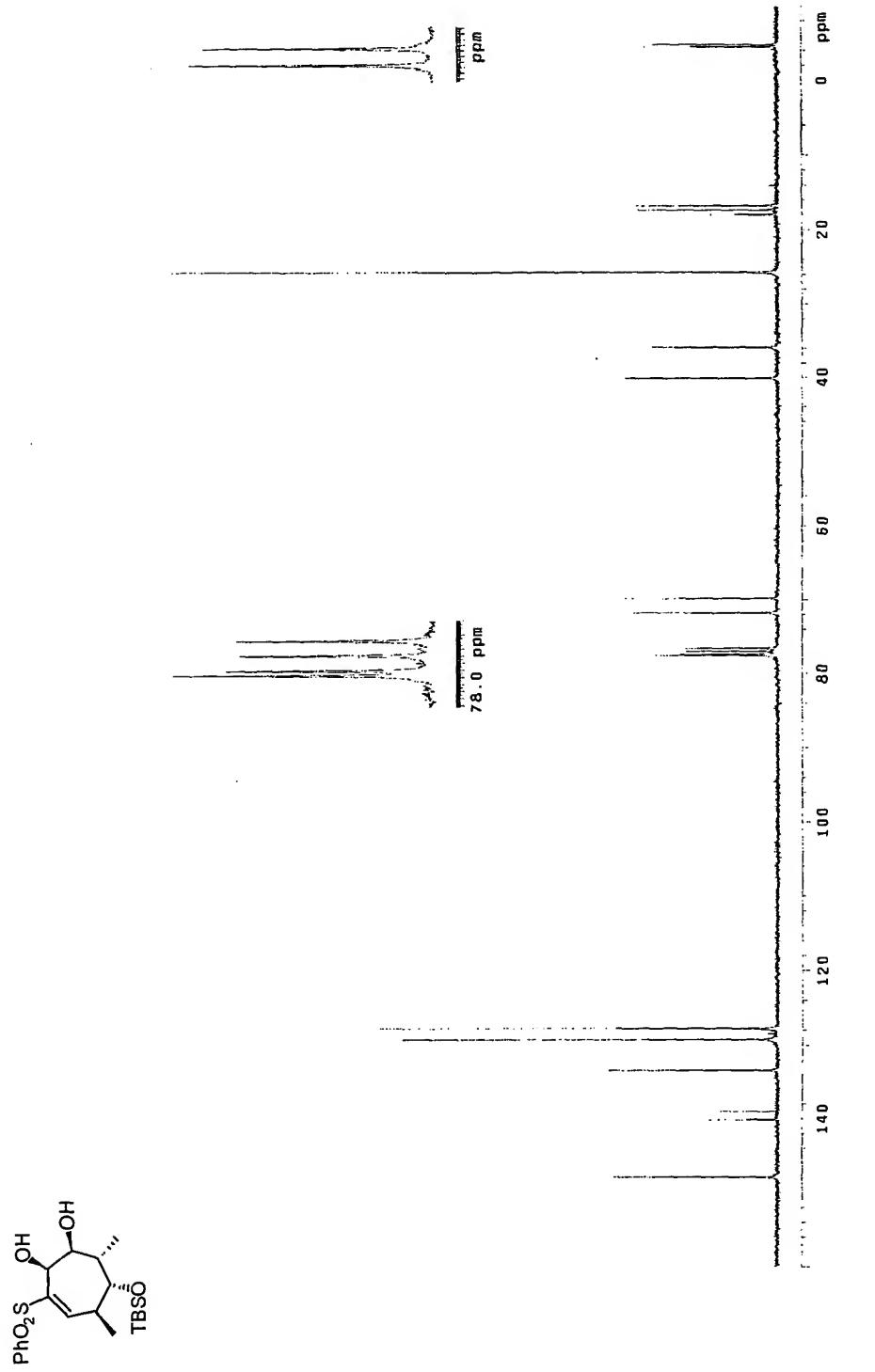
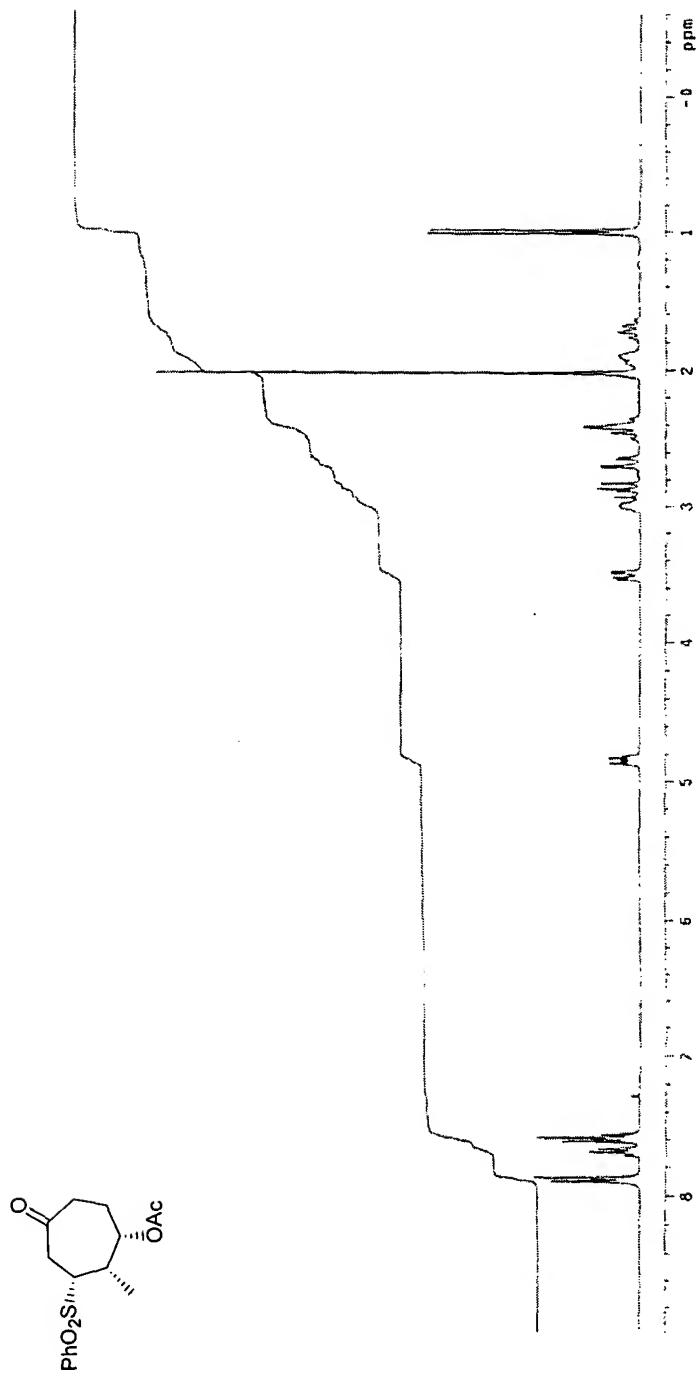


FIGURE 8 (Cont'd)



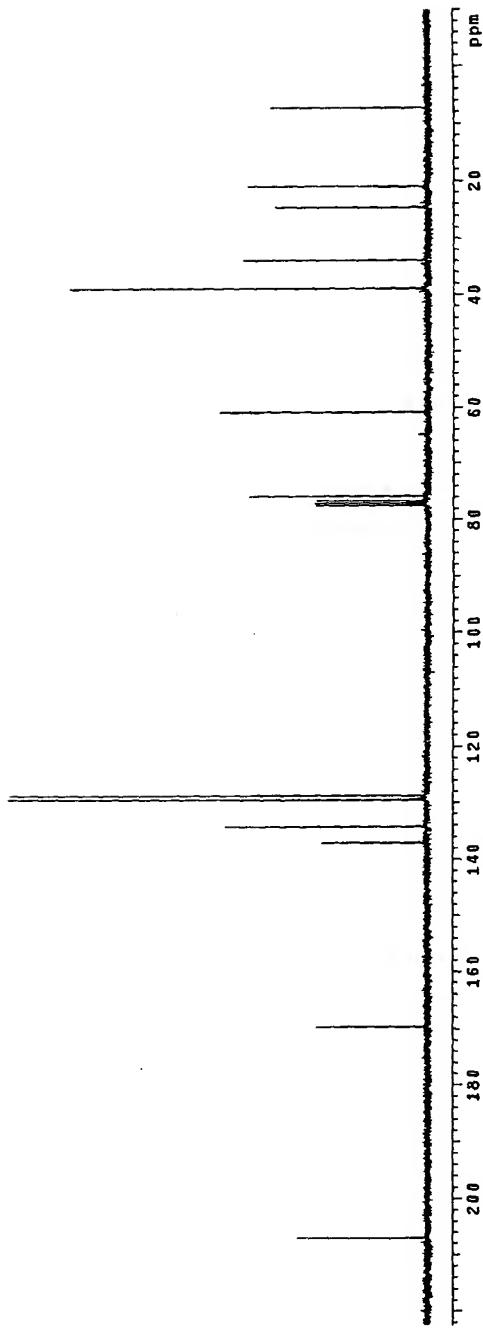
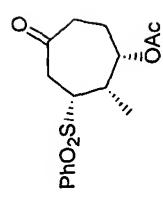
75MHz ^{13}C NMR of compound 39 in CDCl_3

FIGURE 8 (Cont'd)



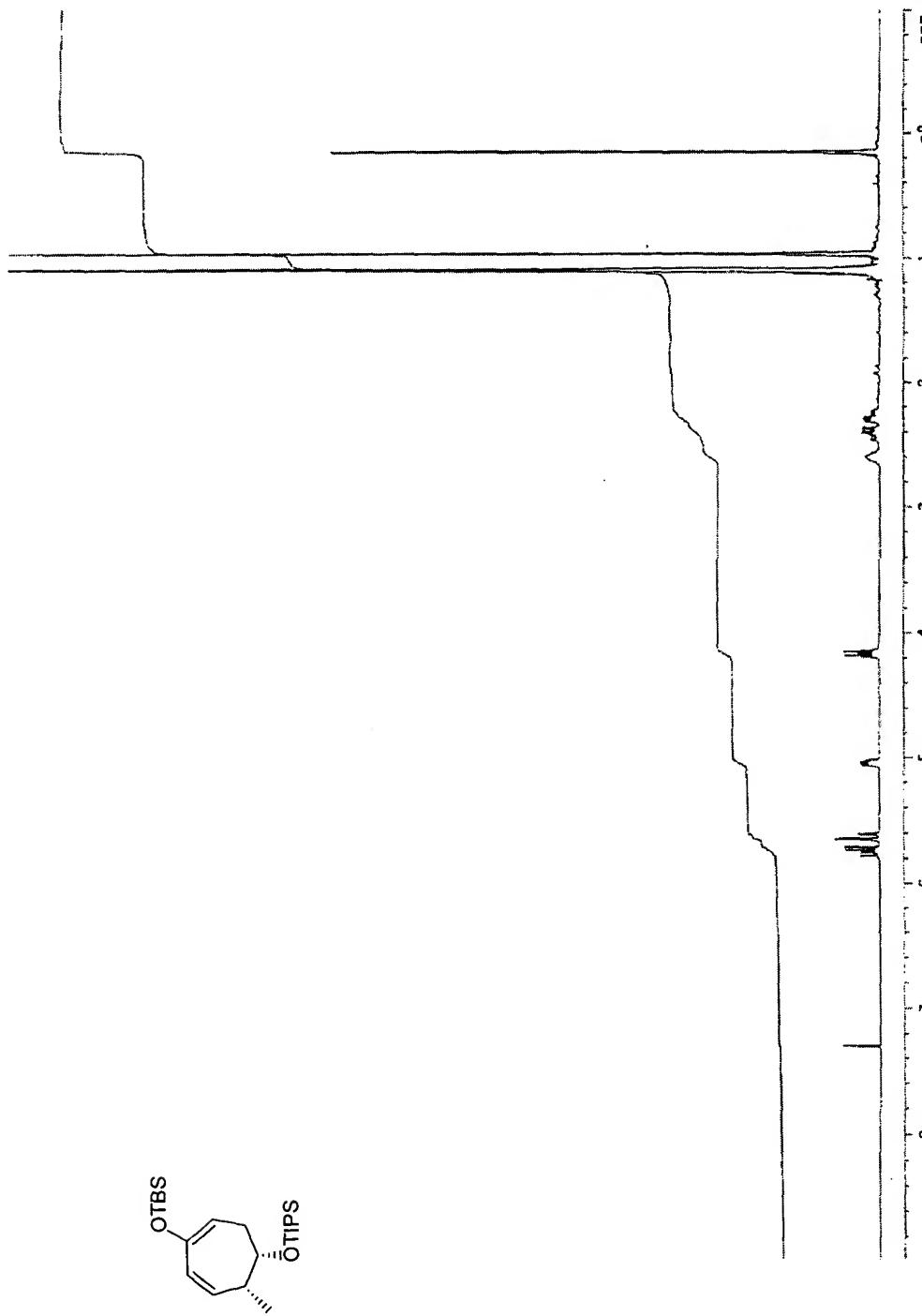
300MHz ^1H NMR of compound 41 in CDCl_3

FIGURE 8 (Cont'd)



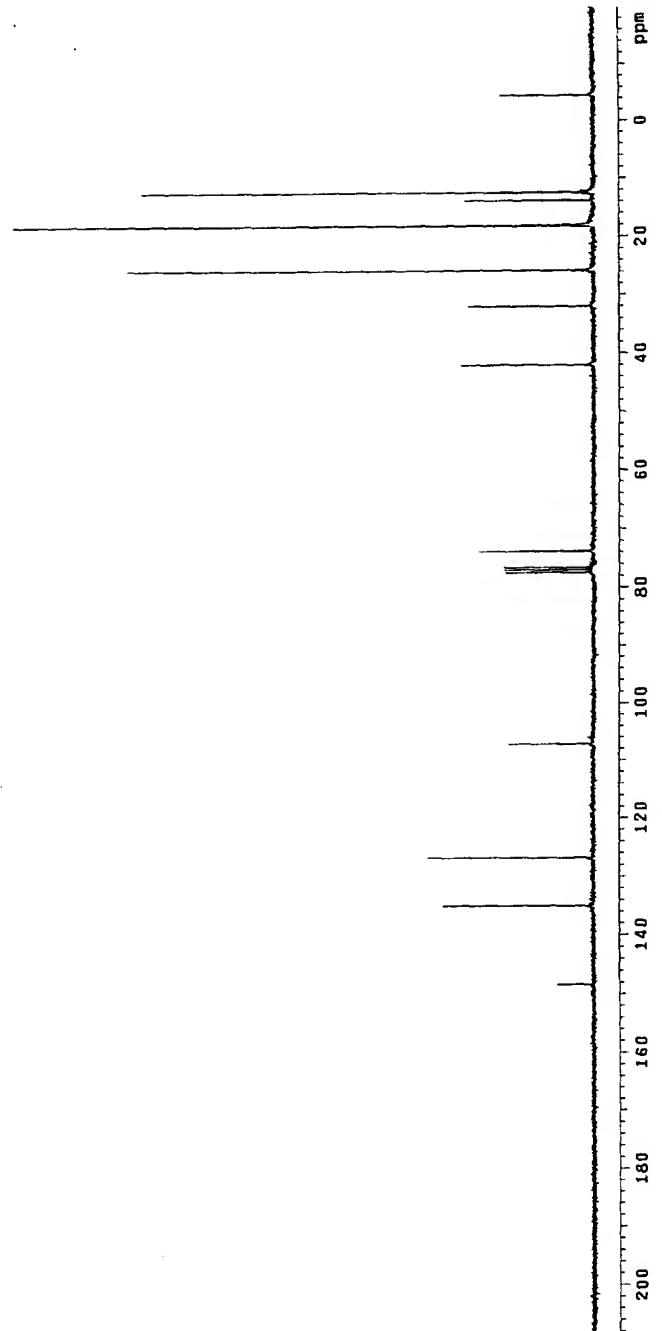
75MHz ^{13}C NMR of compound 41 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 42 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 42 in CDCl_3

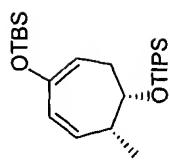
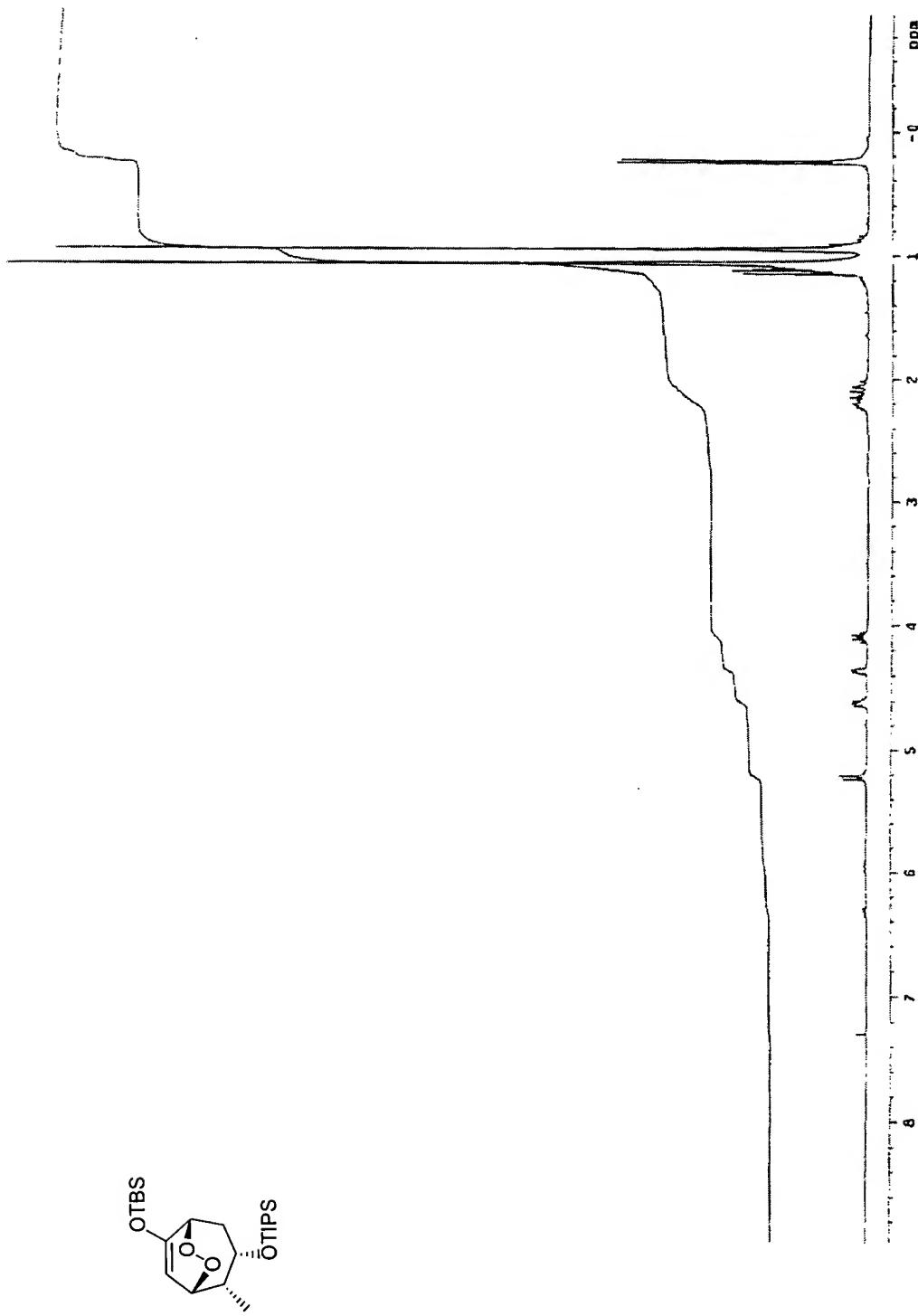
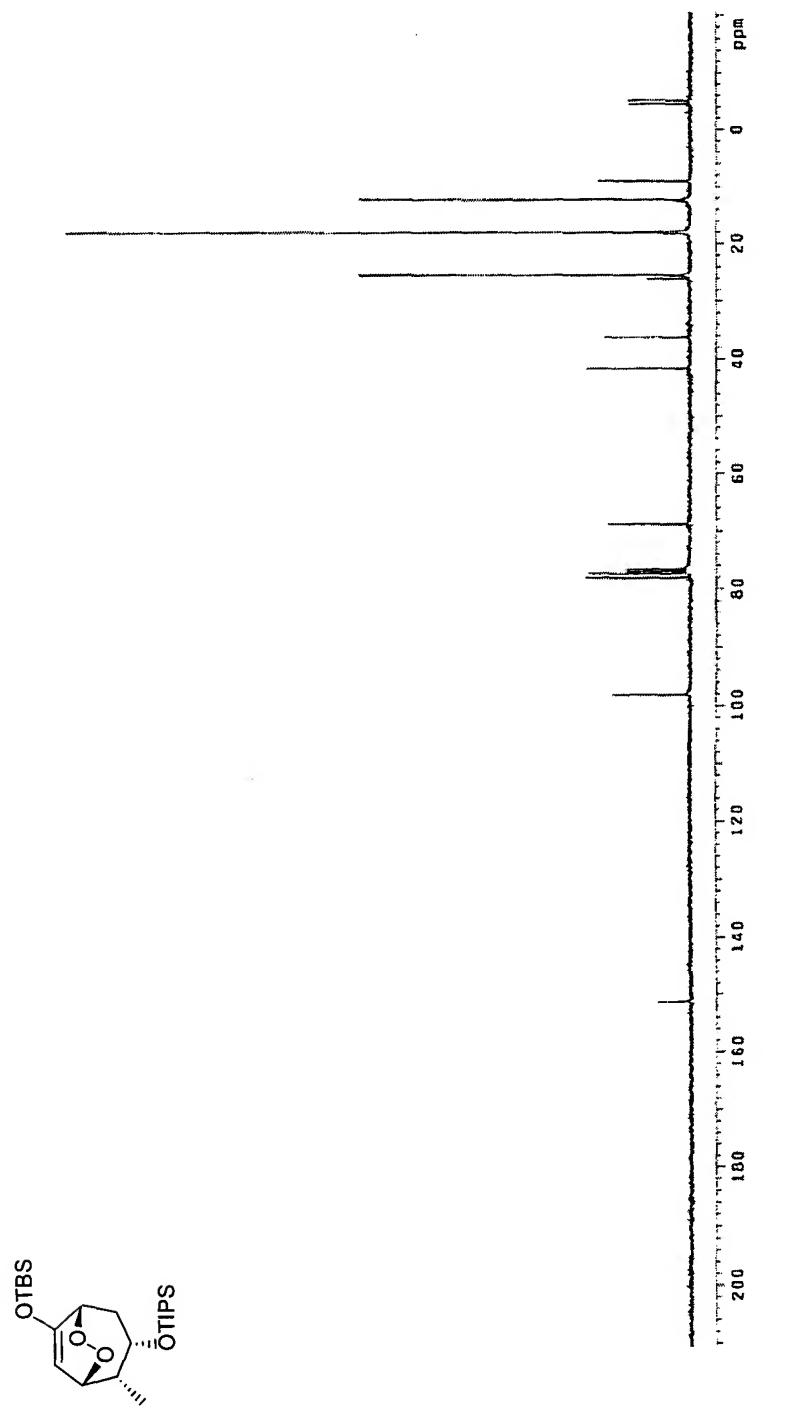


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 43 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 43 in CDCl_3

FIGURE 8 (Cont'd)

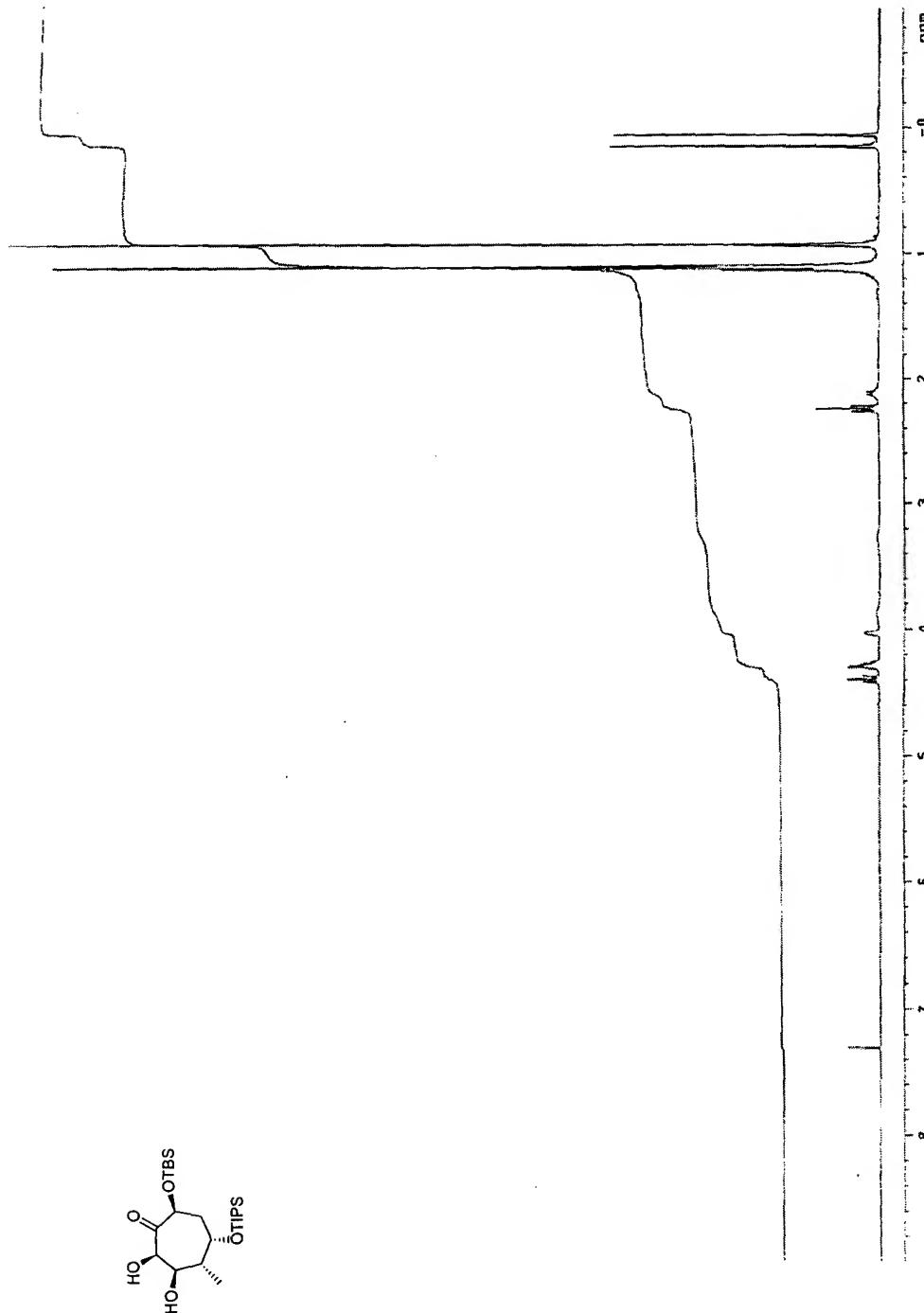
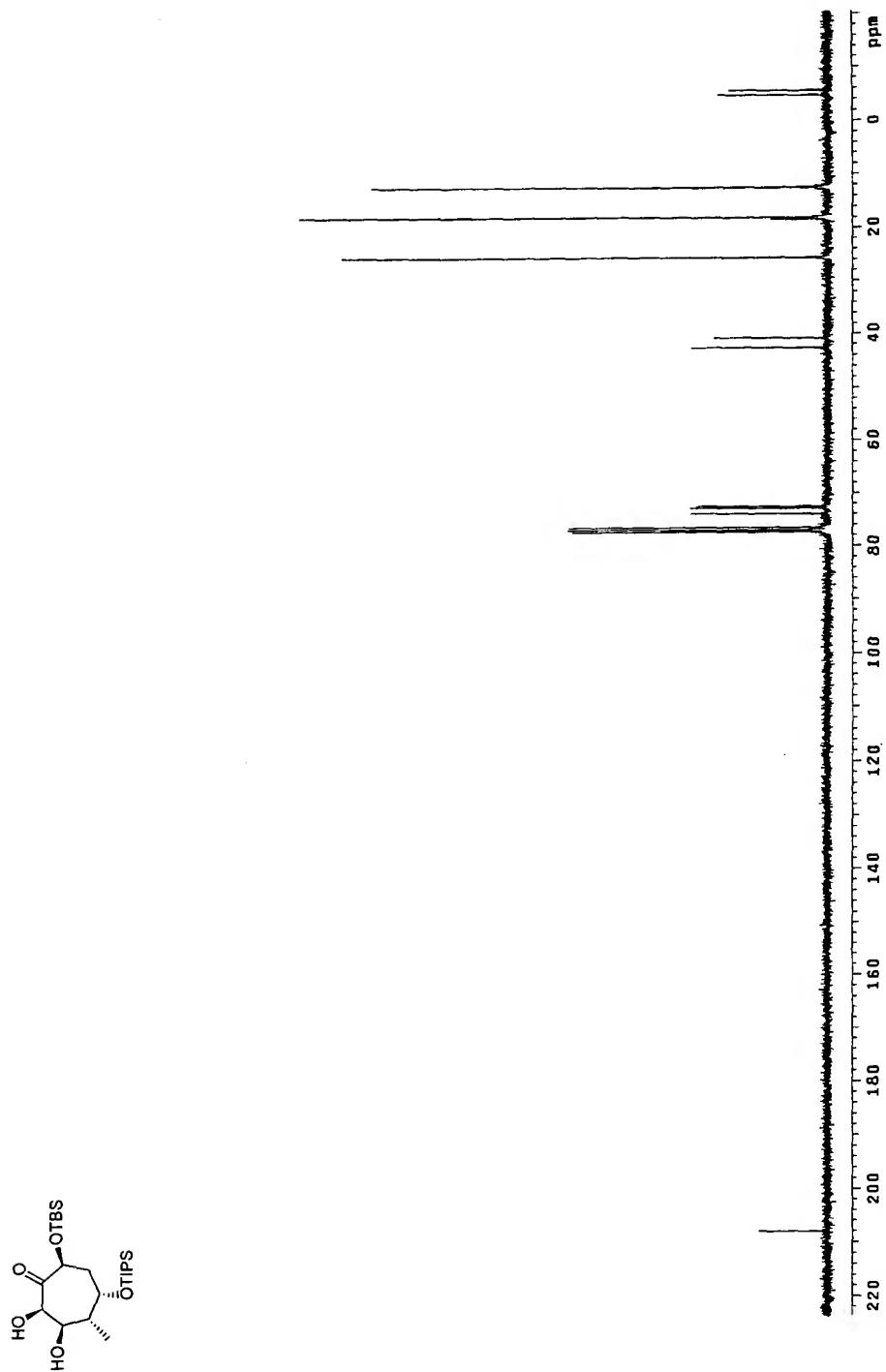


FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 46 in CDCl_3

FIGURE 8 (Cont'd)

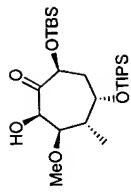
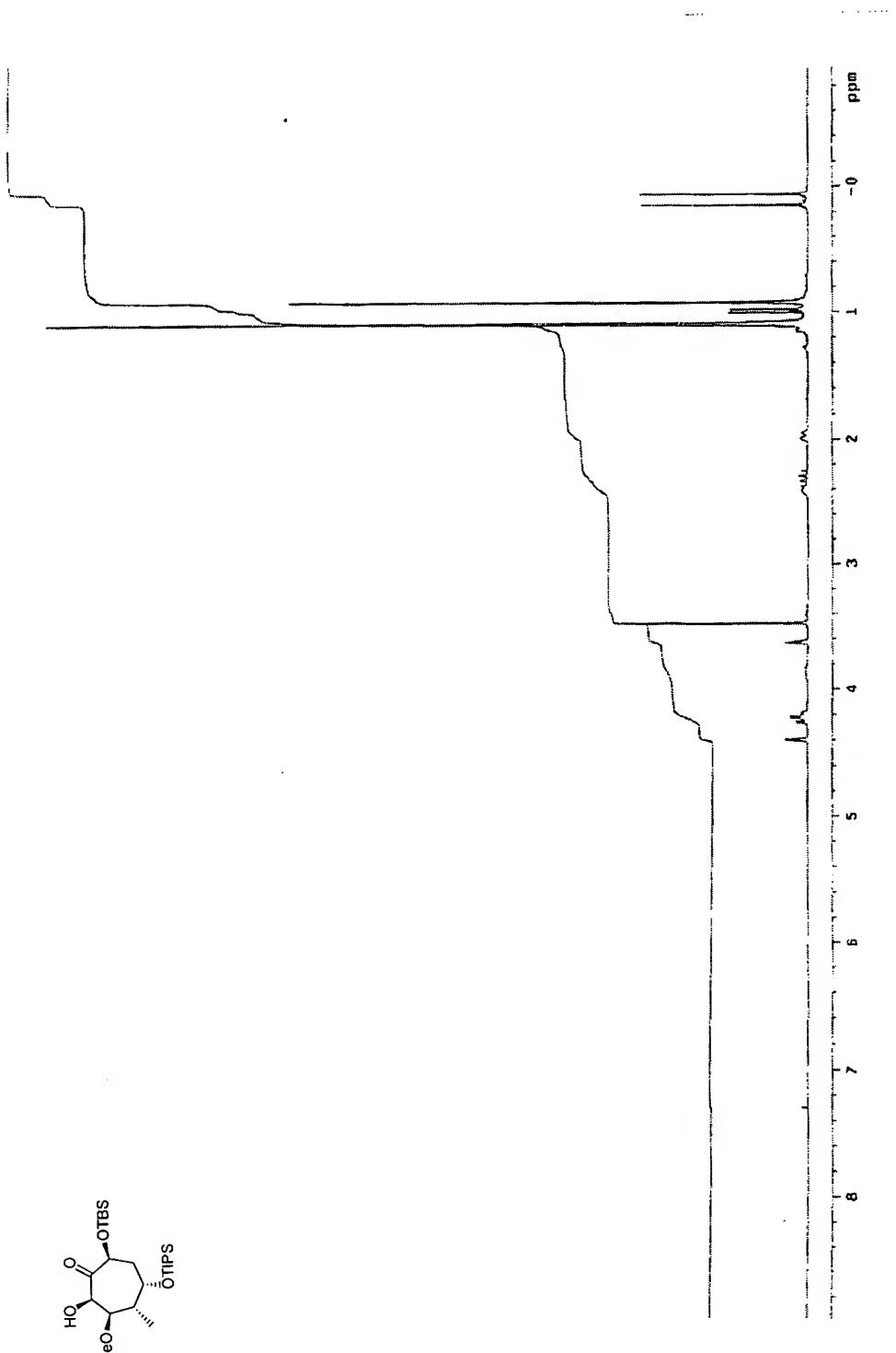


FIGURE 8 (Cont'd)

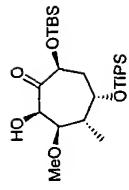
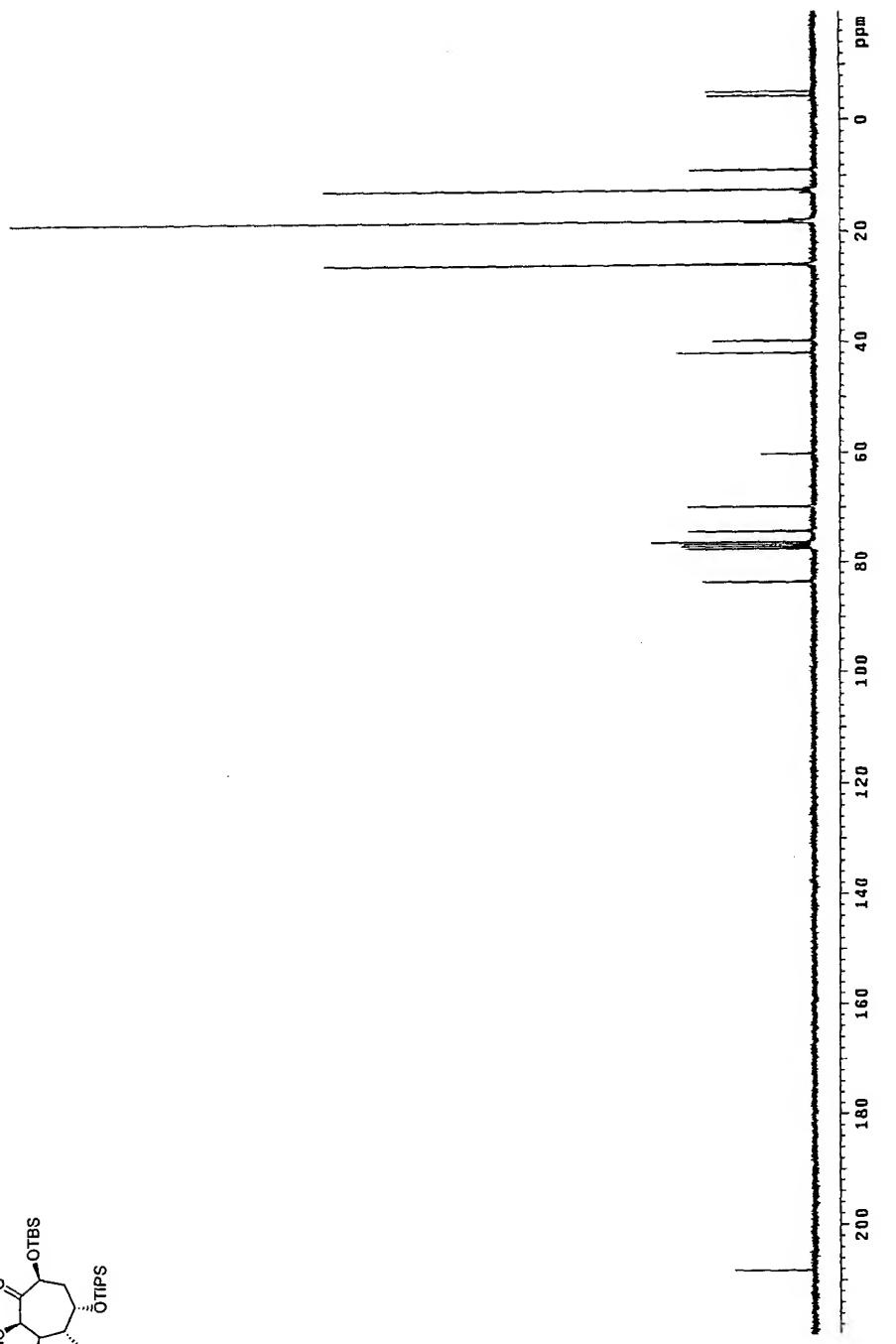
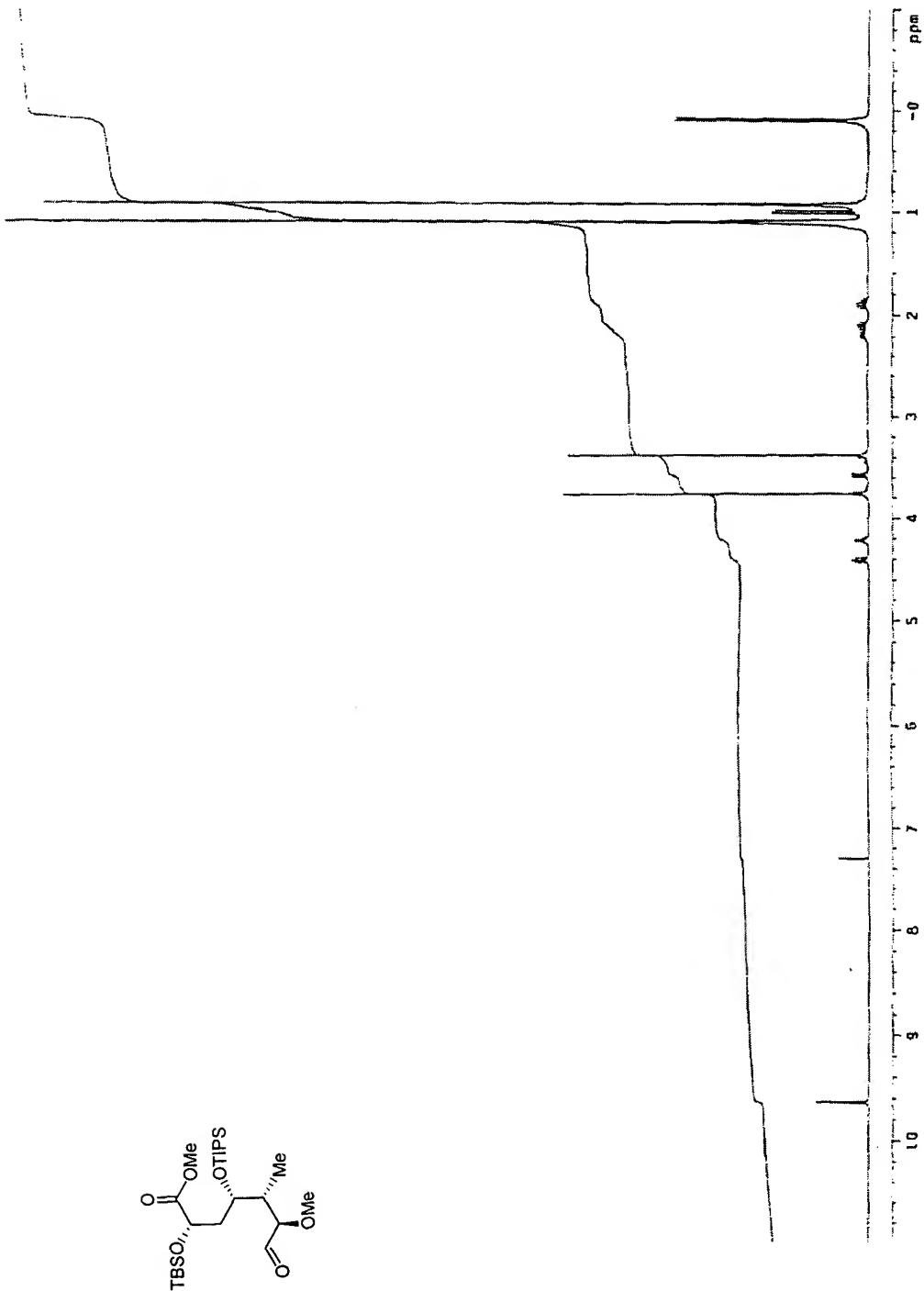


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 48 in CDCl_3

FIGURE 8 (Cont'd)

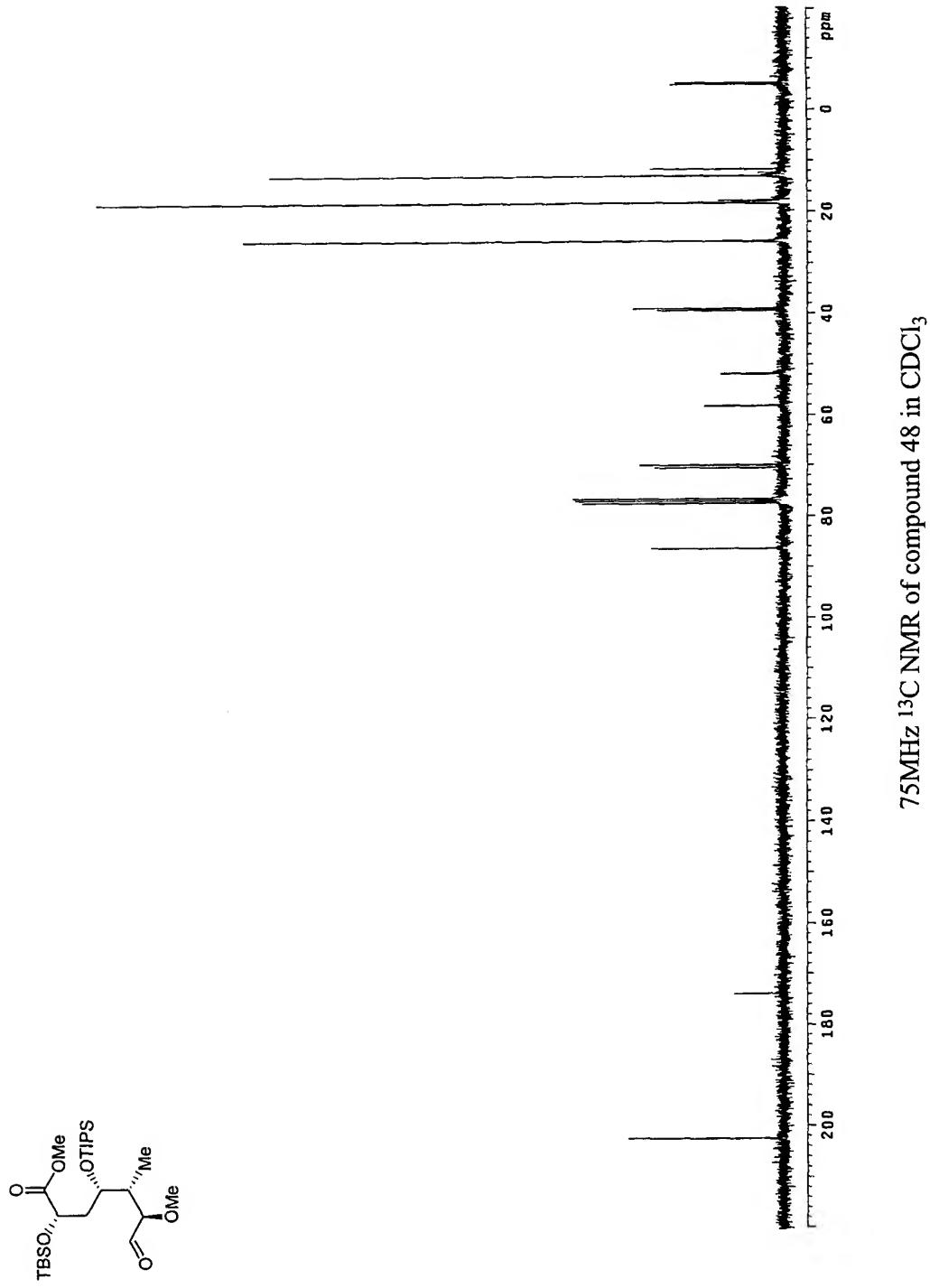
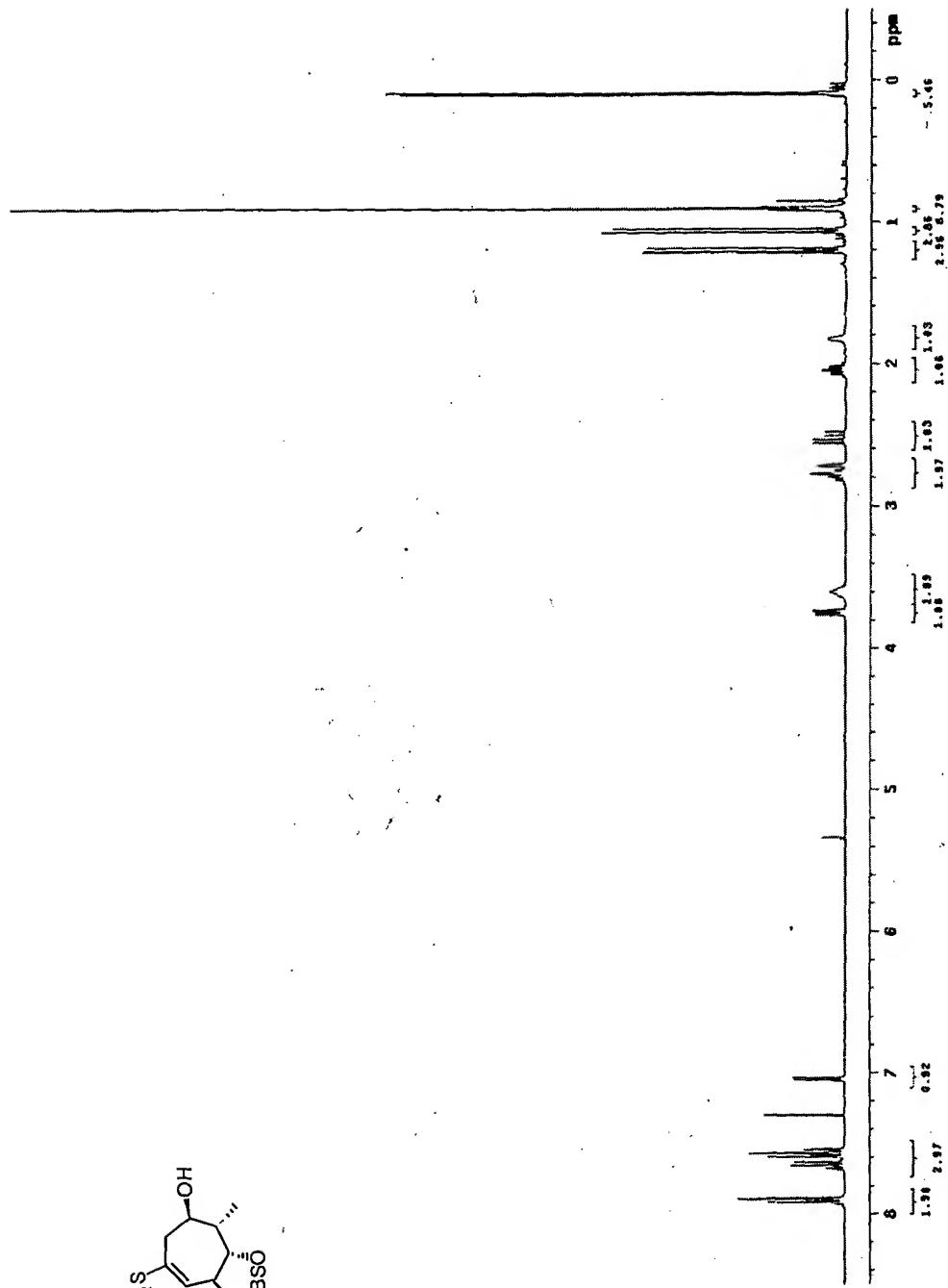
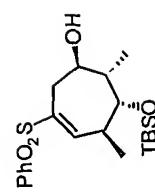


FIGURE 8 (Cont'd)



300MHz ¹H NMR of compound 56 in CDCl_3

FIGURE 8 (Cont'd)

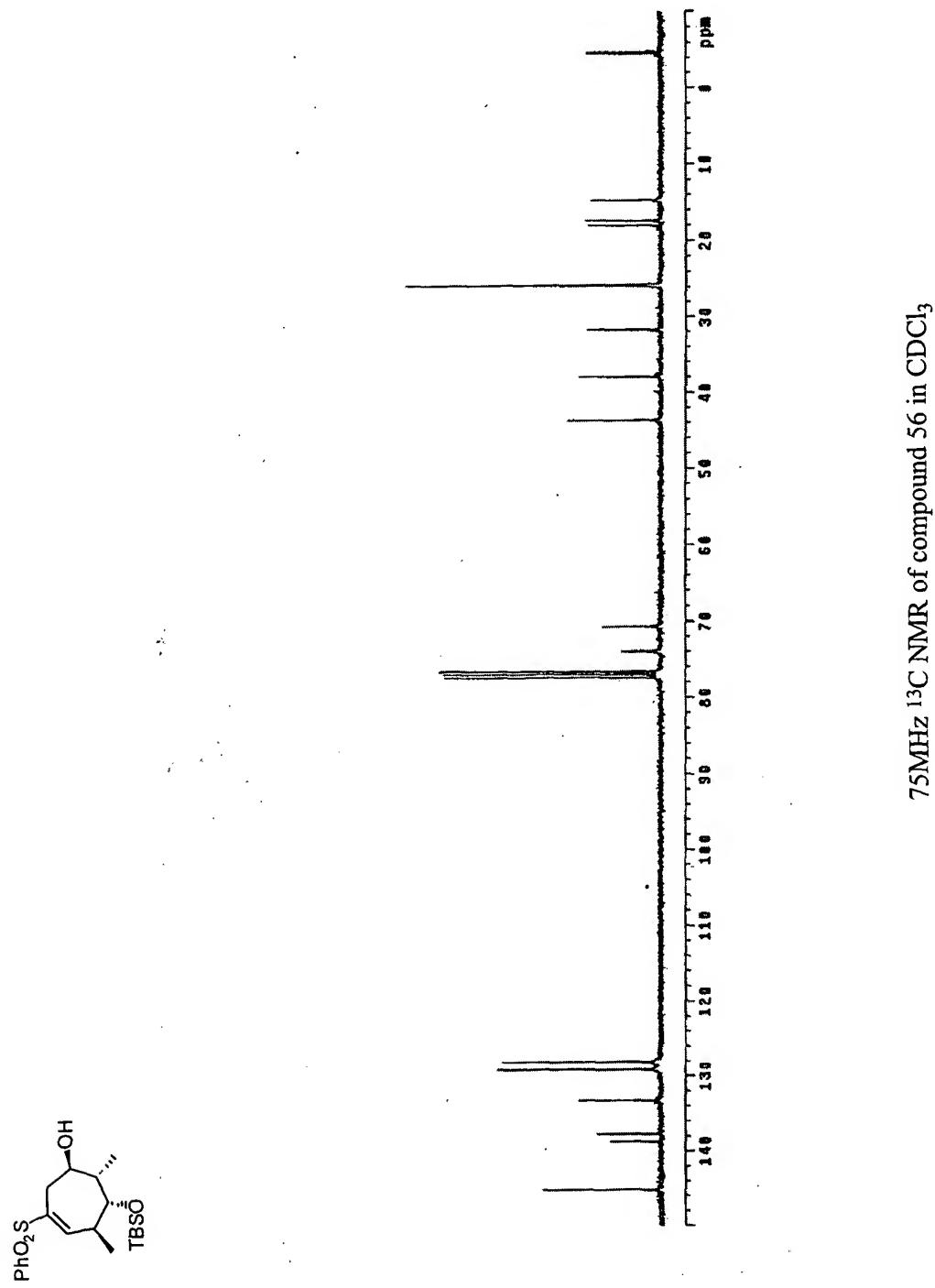
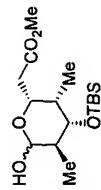
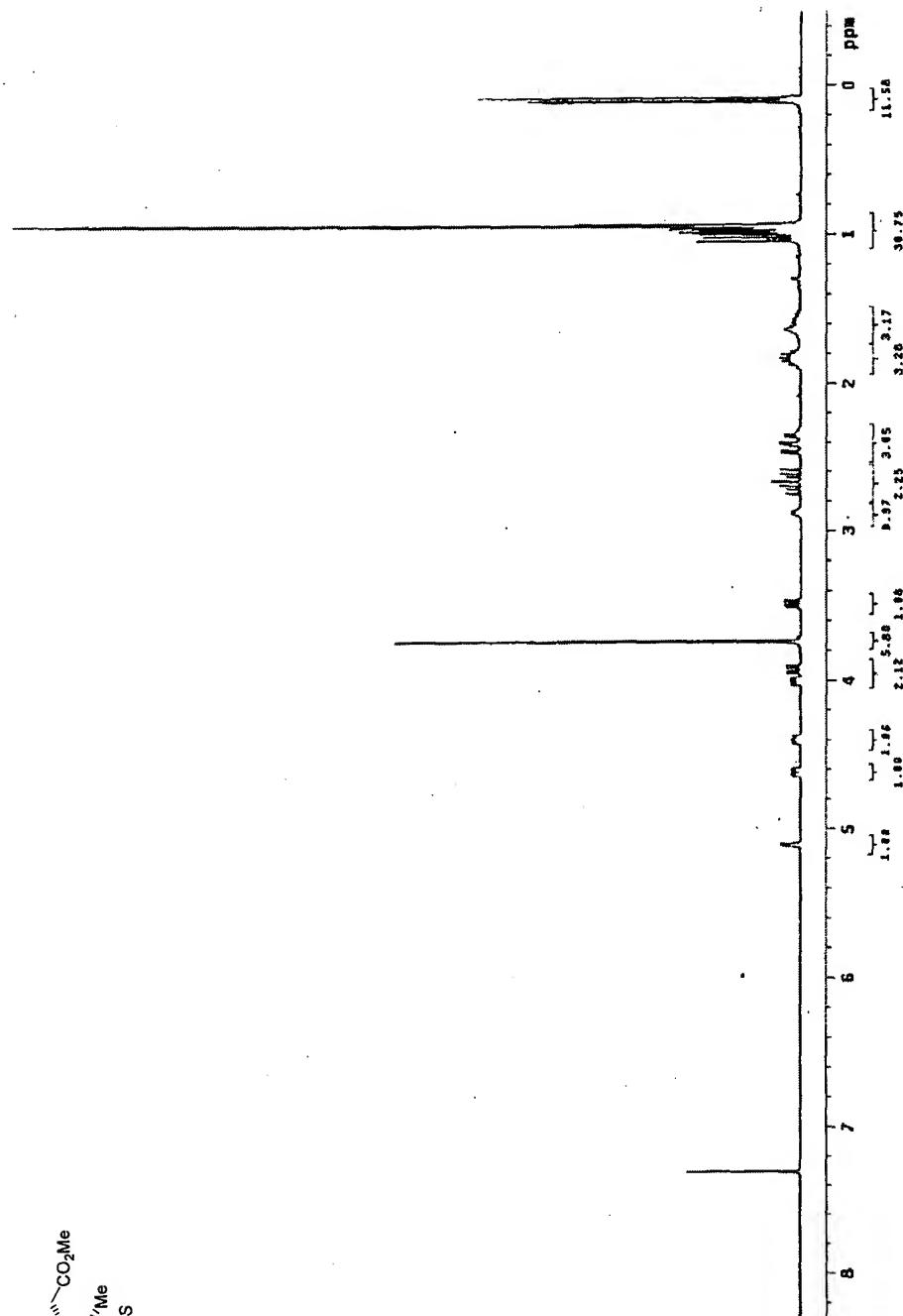
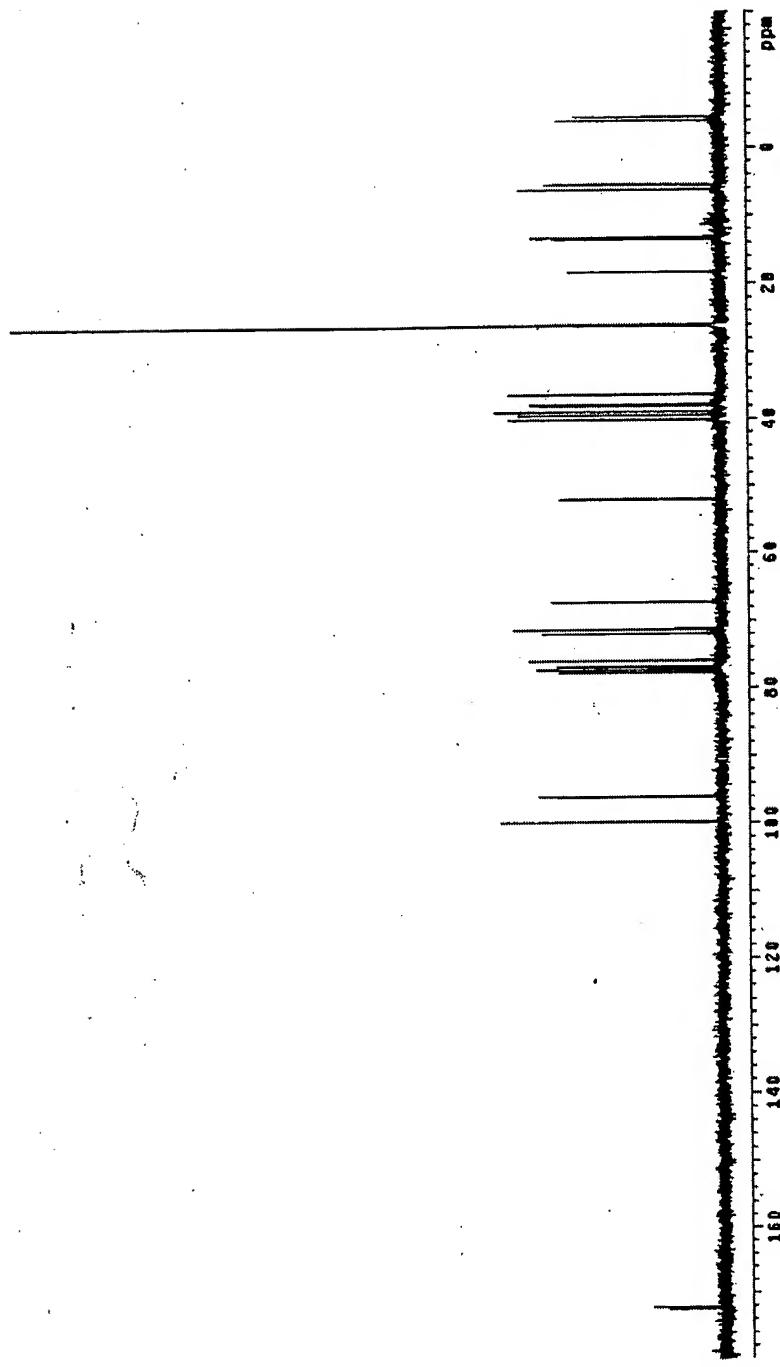


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 57 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 57 in CDCl_3

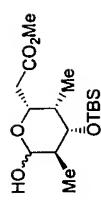
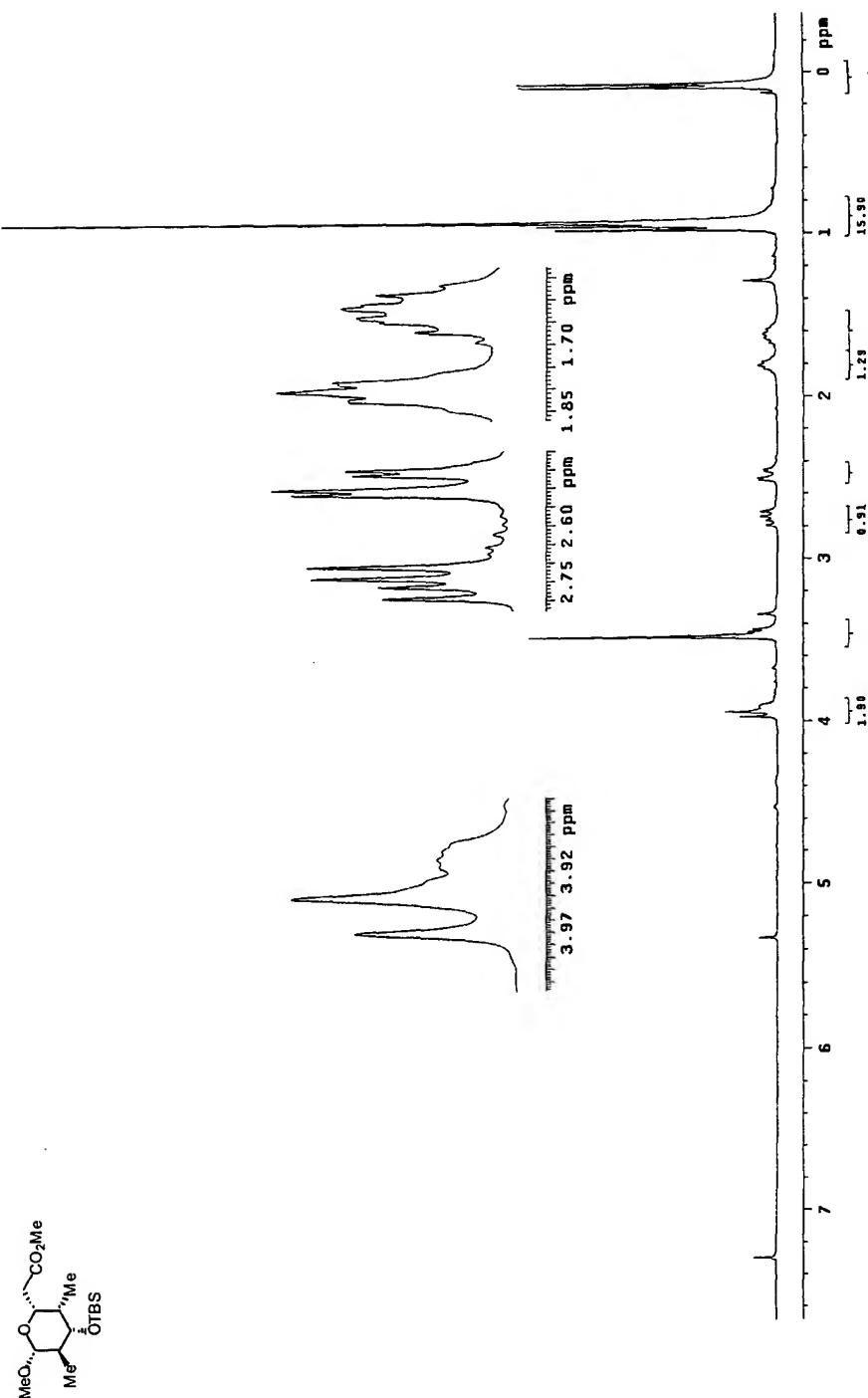
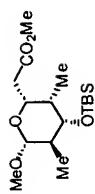
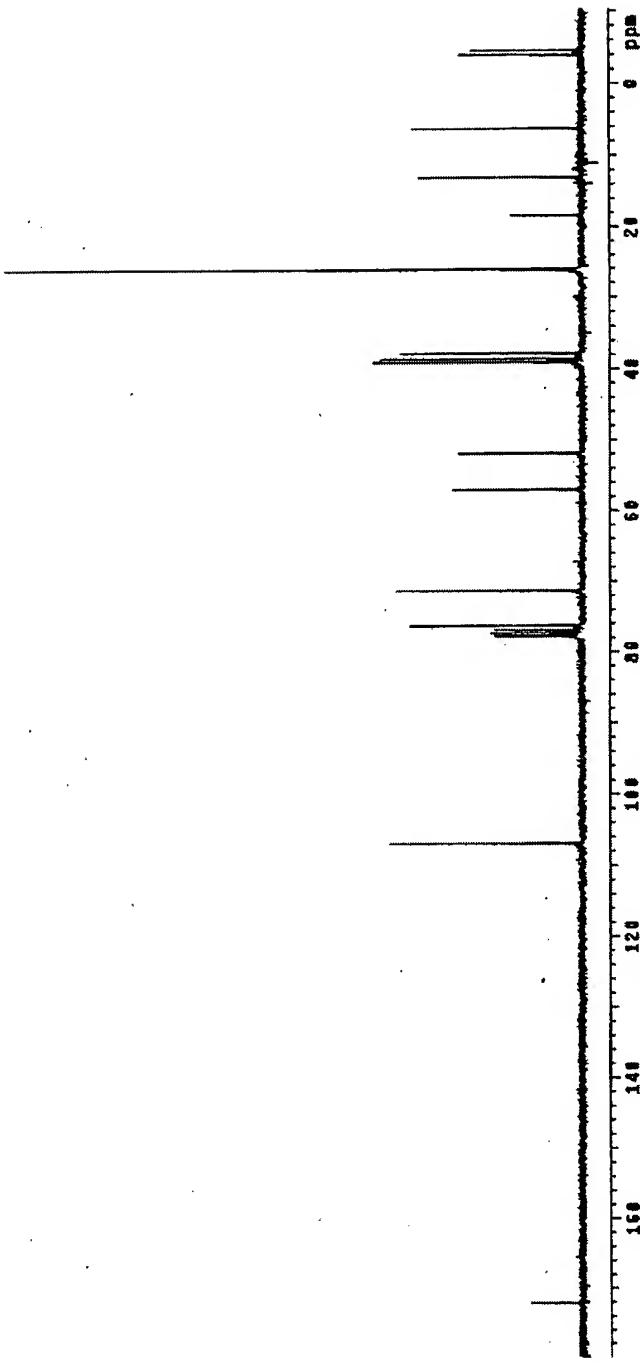


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 58 α in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 58α in CDCl_3

FIGURE 8 (Cont'd)

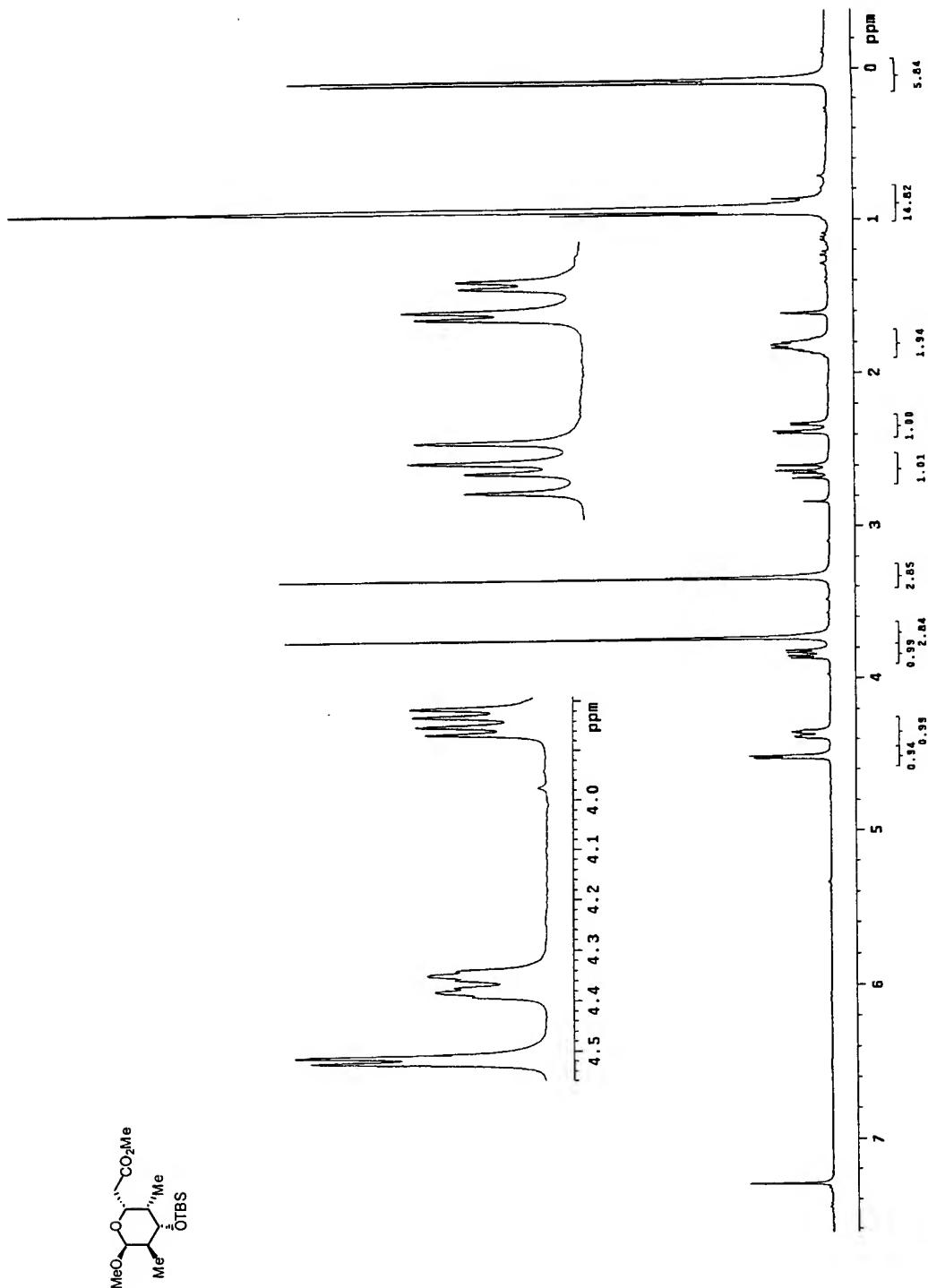


FIGURE 8 (Cont'd)

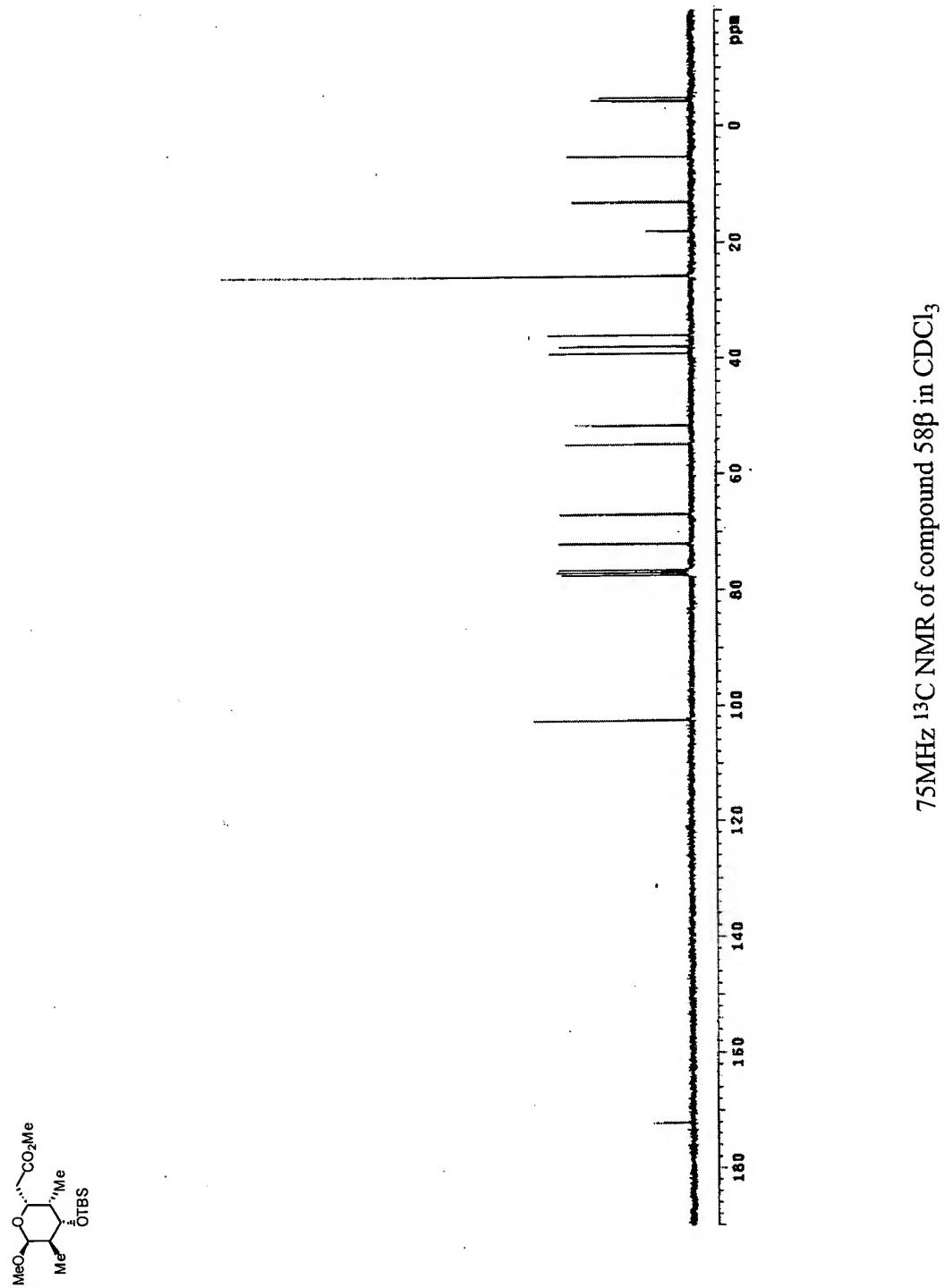
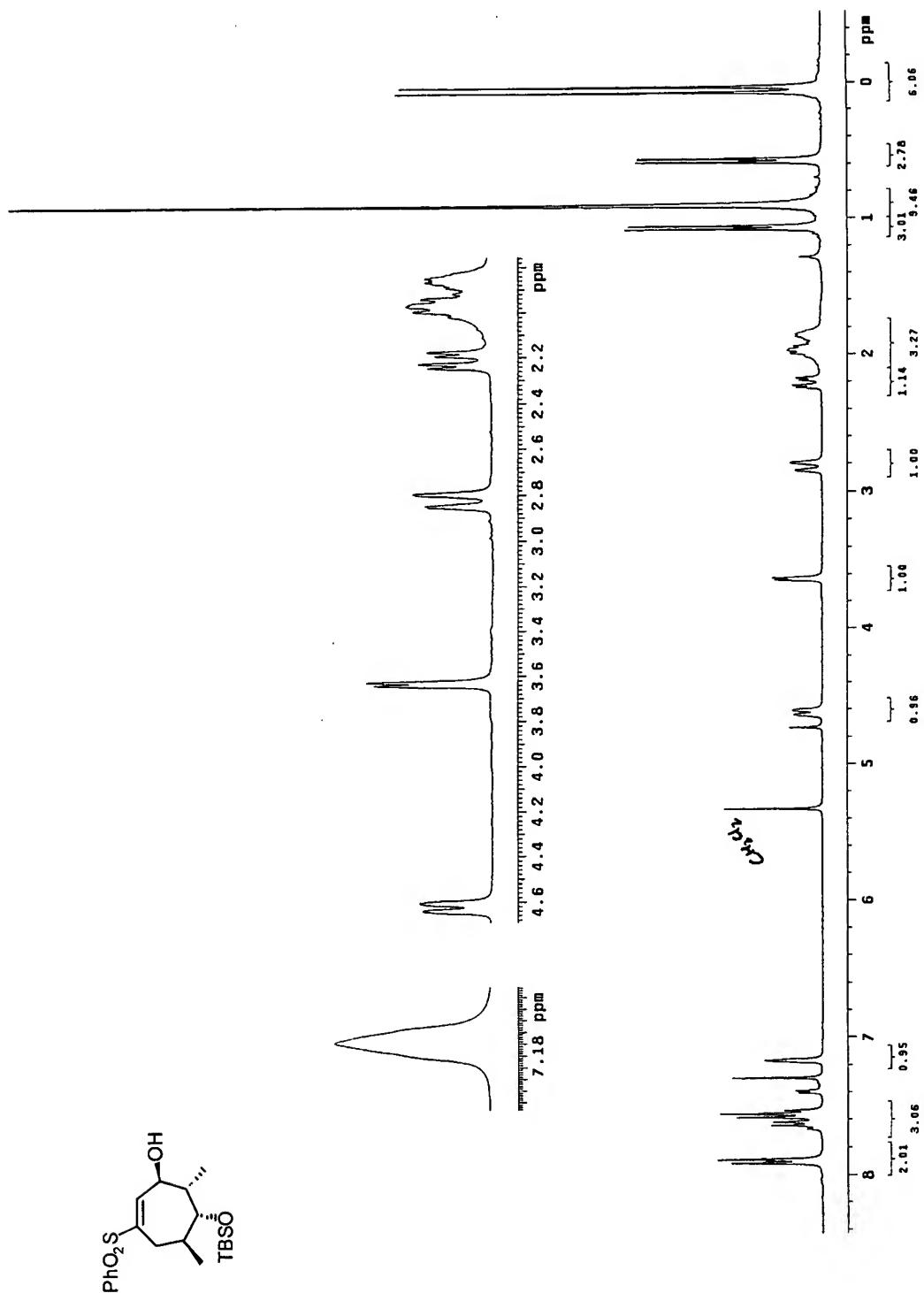


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 59 in CDCl_3

FIGURE 8 (Cont'd)

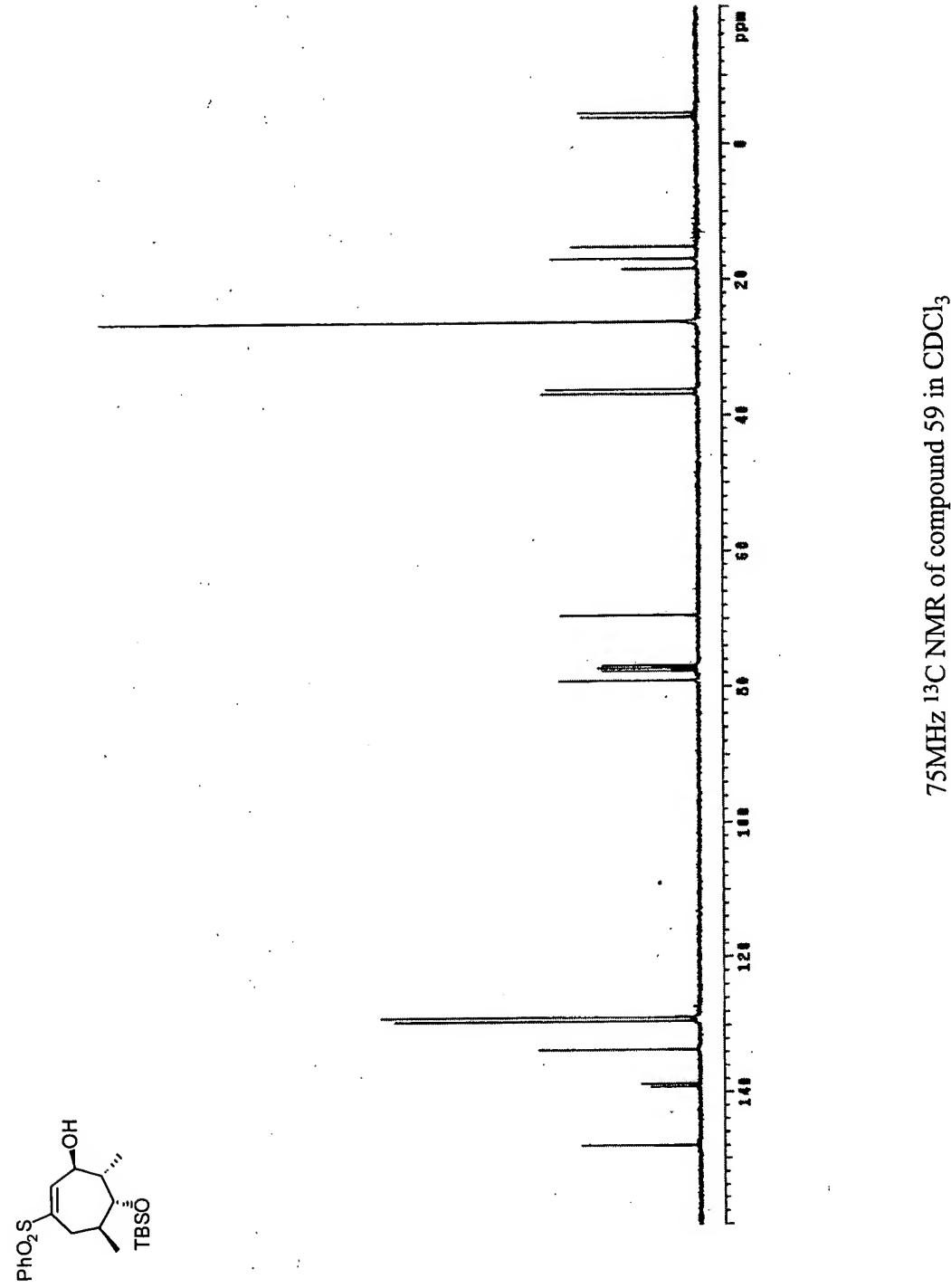


FIGURE 8 (Cont'd)

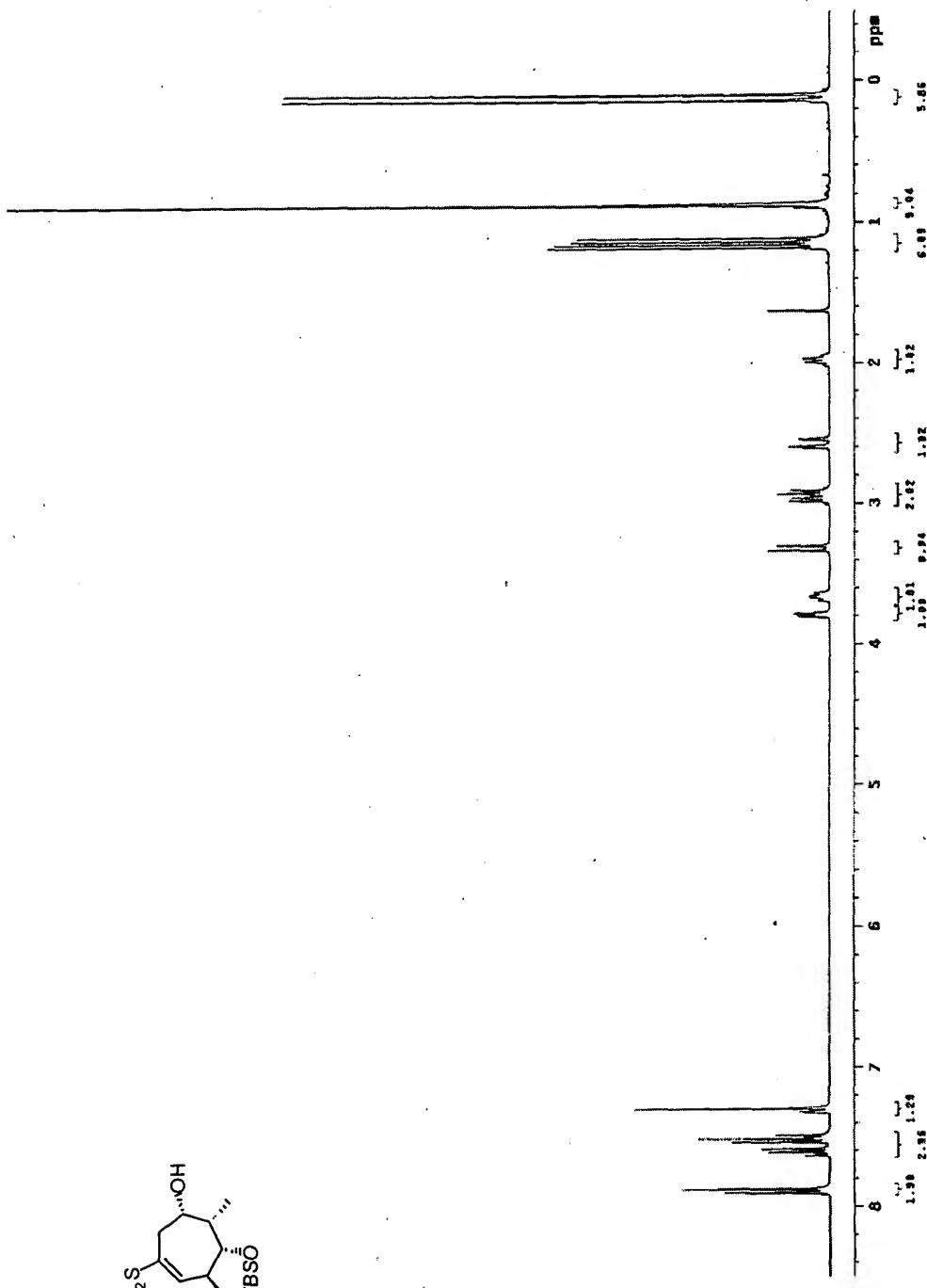
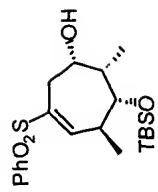
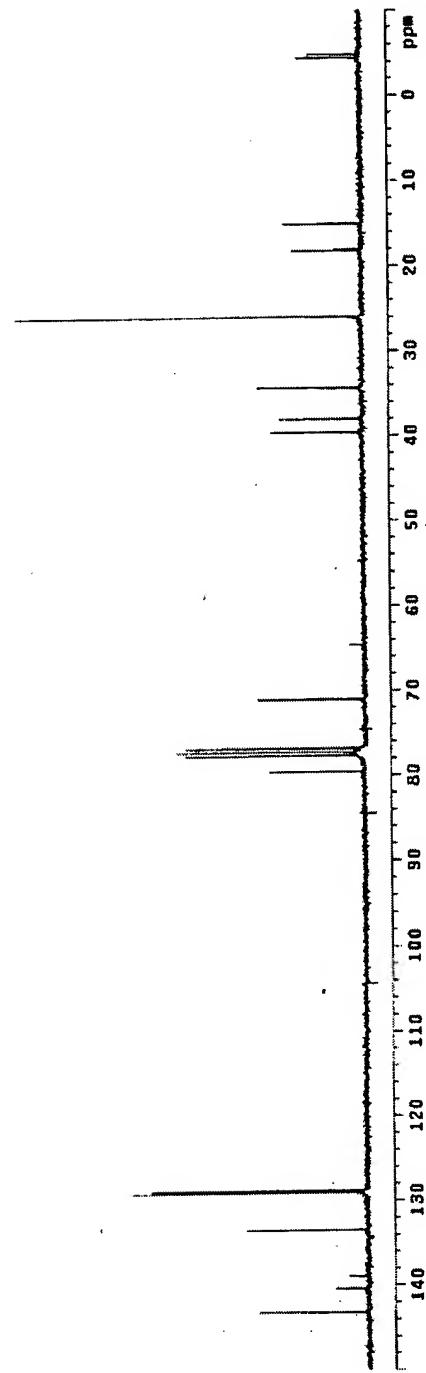
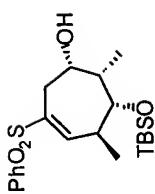


FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 60 in CDCl_3

FIGURE 8 (Cont'd)

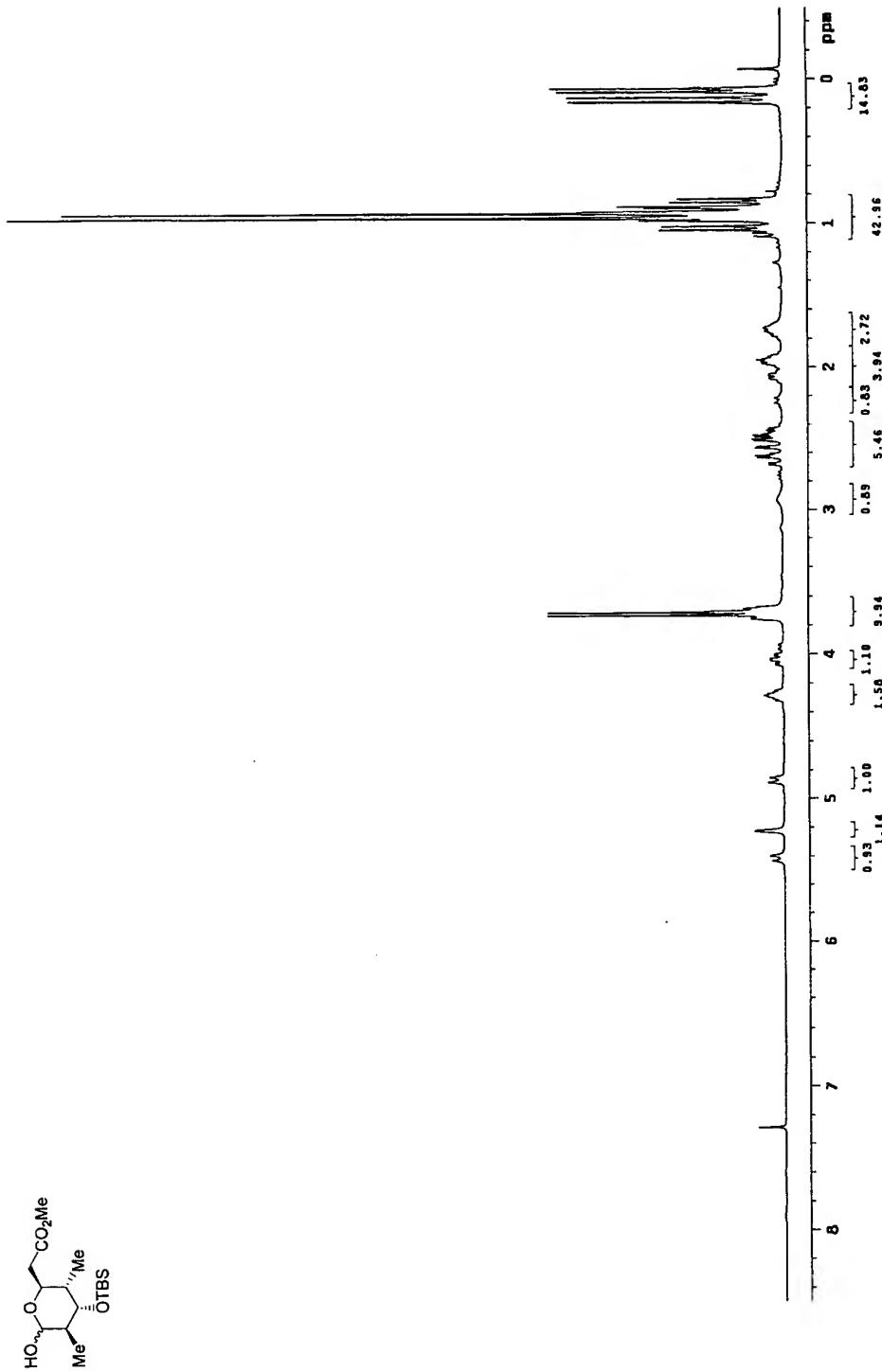


FIGURE 8 (Cont'd)

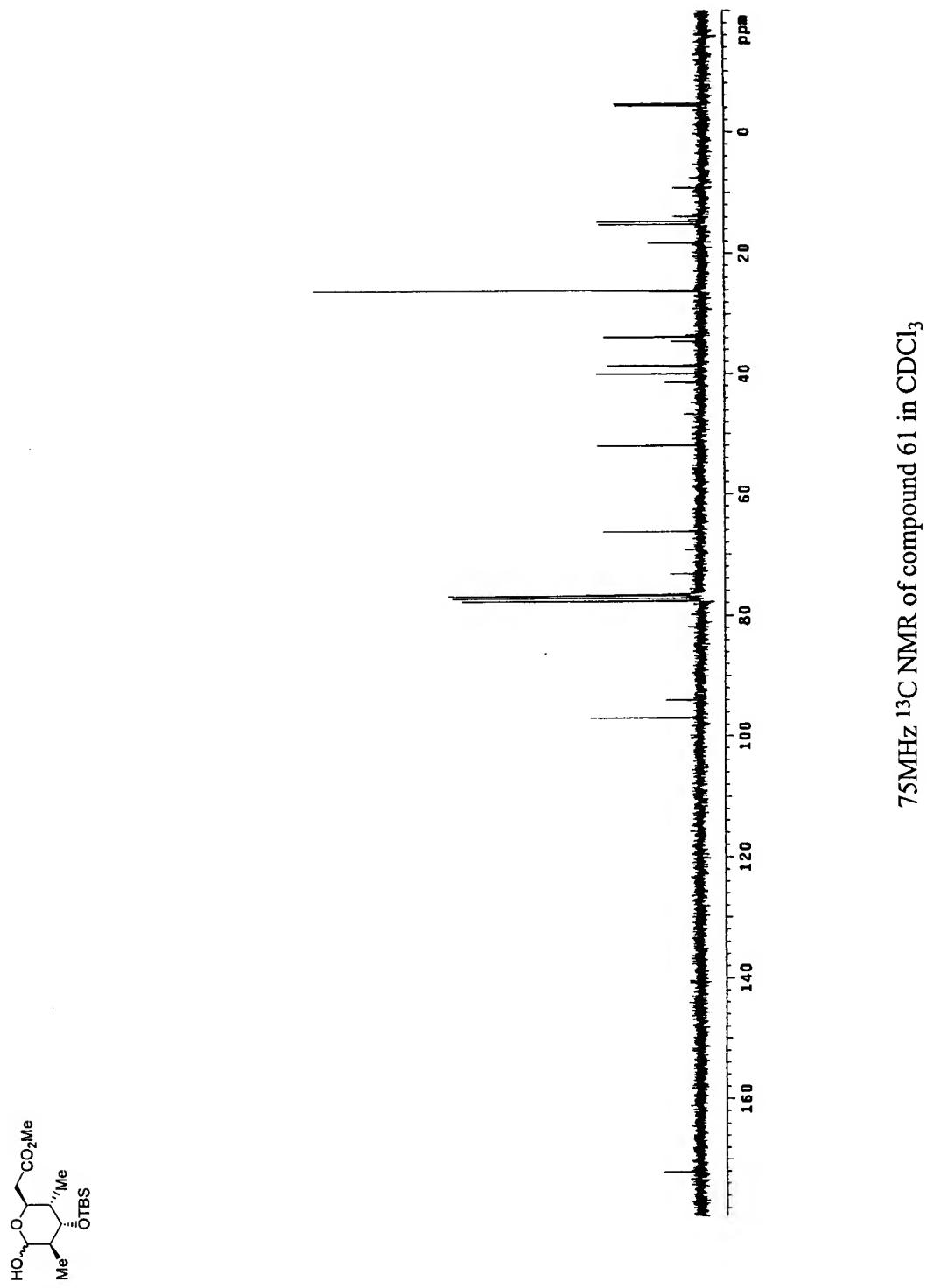
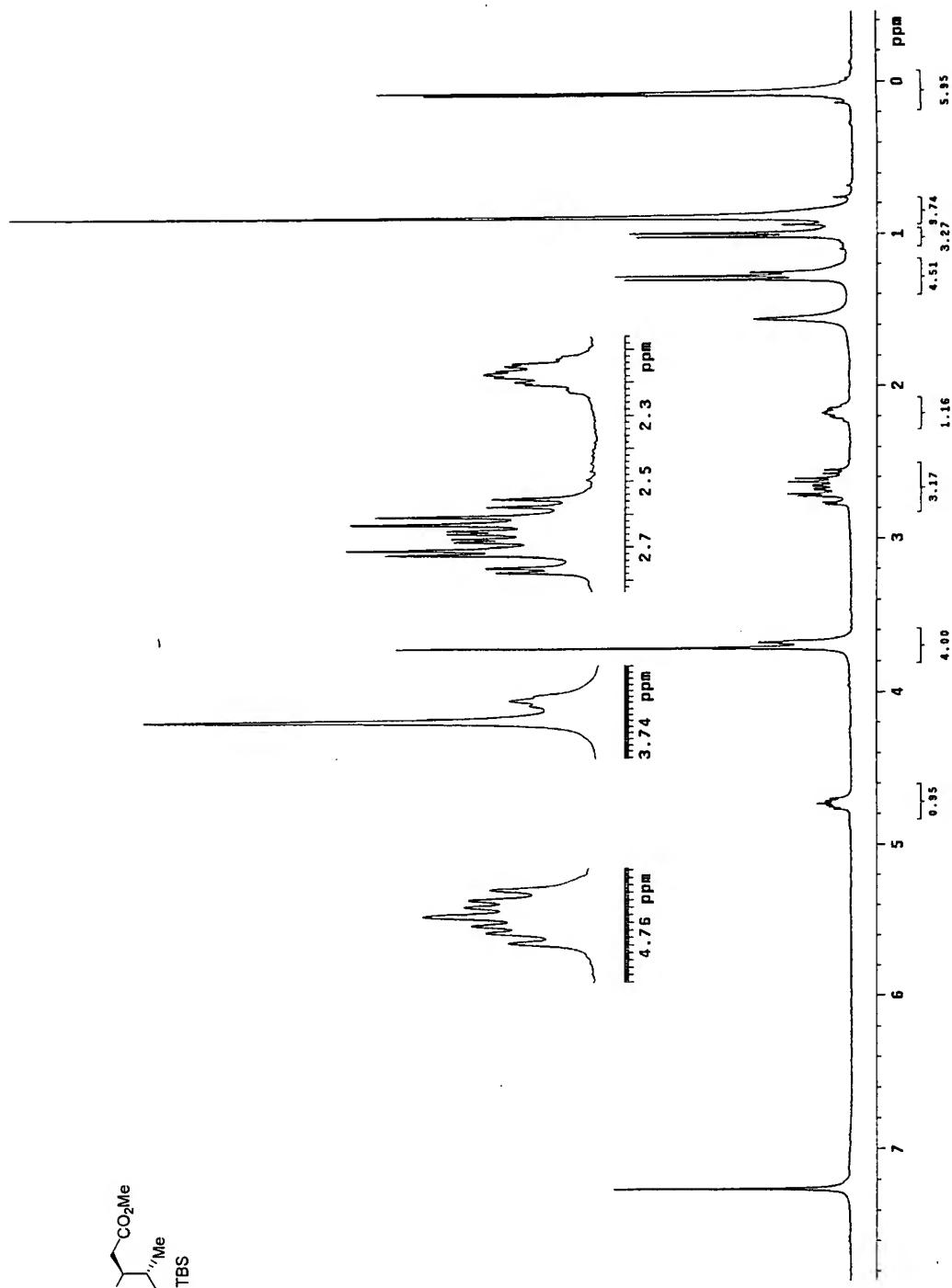
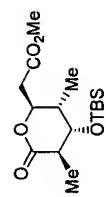
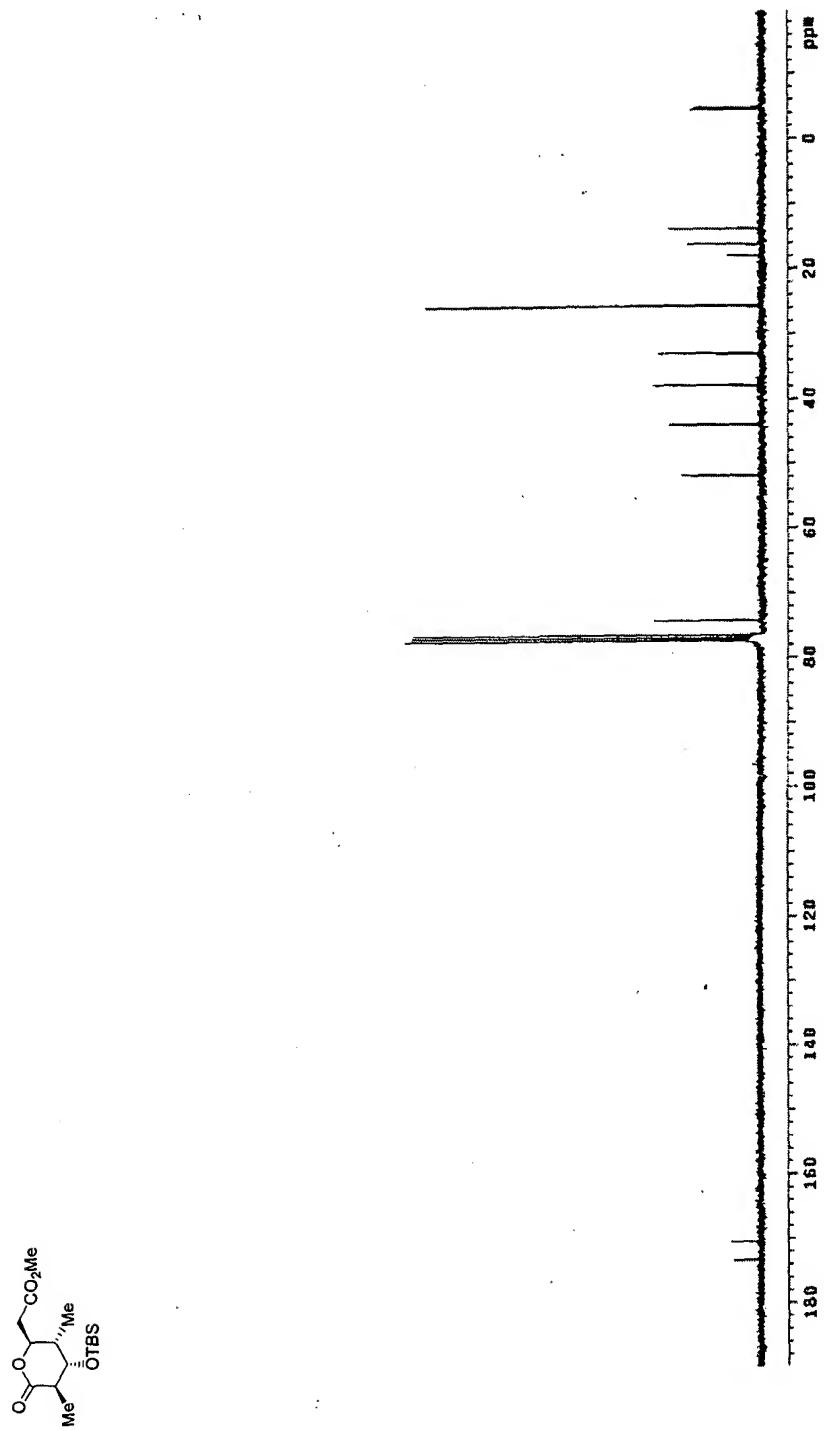


FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 62 in CDCl_3

FIGURE 8 (Cont'd)



75 MHz ^{13}C NMR of compound 62 in CDCl_3

FIGURE 8 (Cont'd)

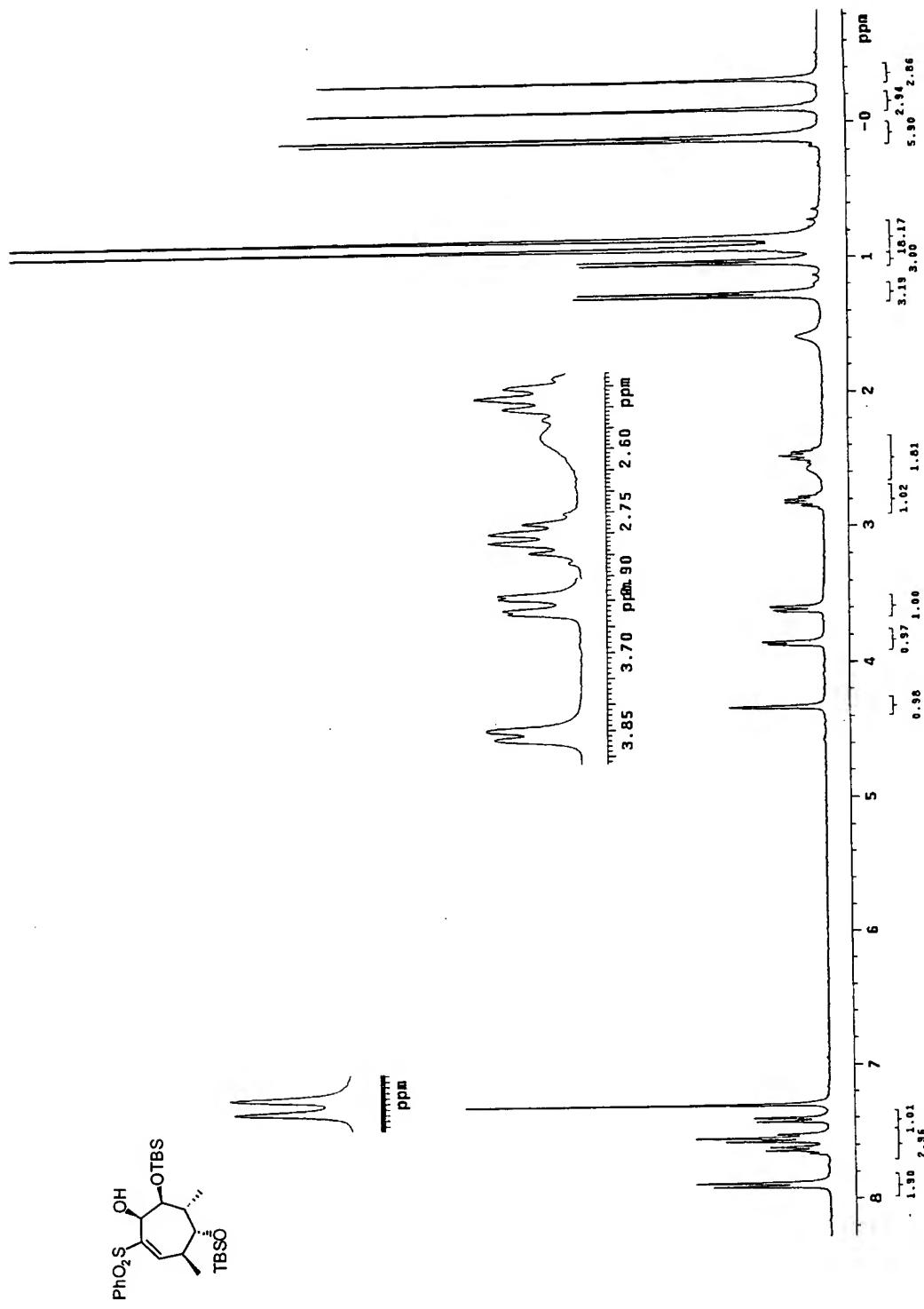
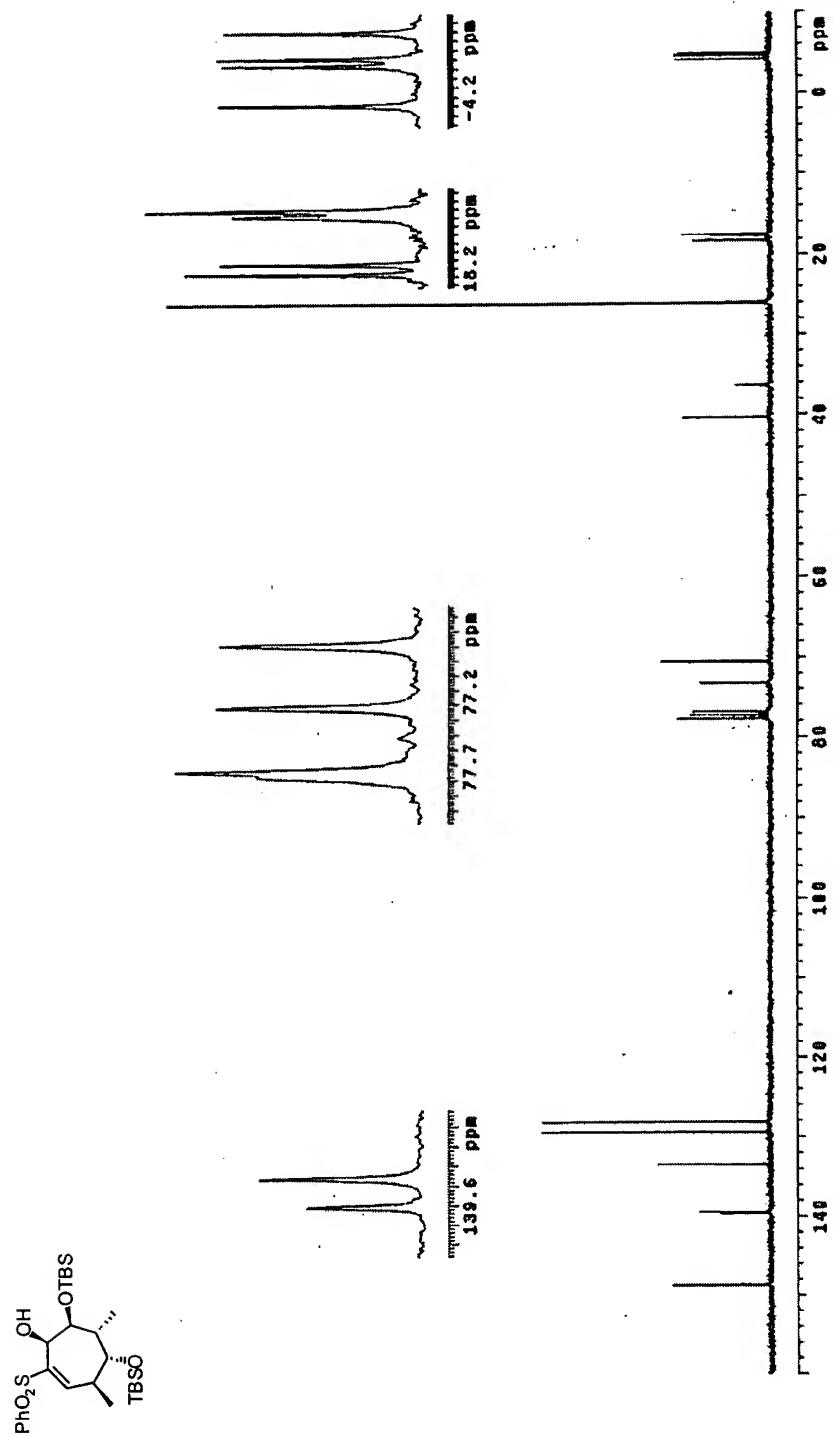
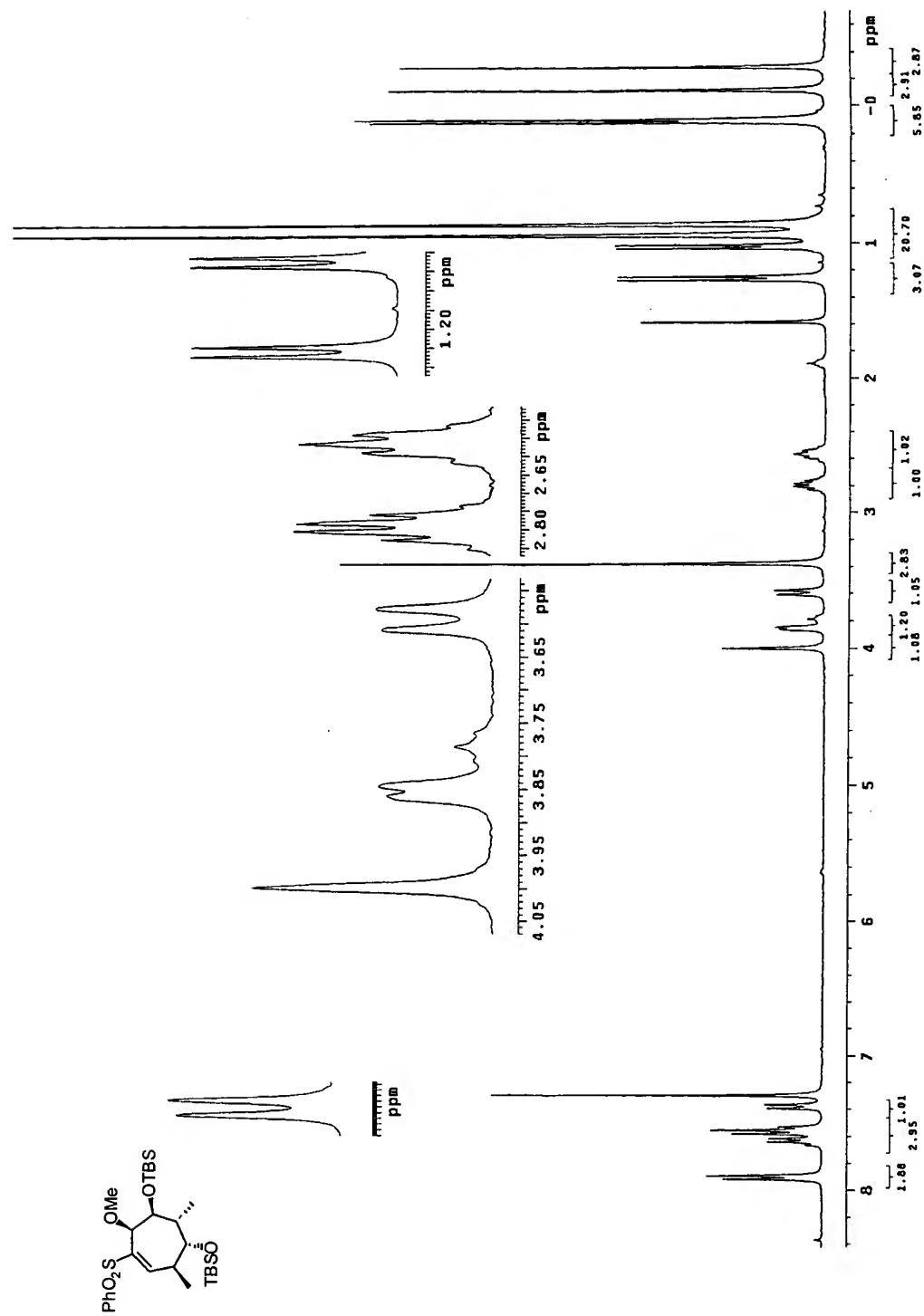


FIGURE 8 (Cont'd)



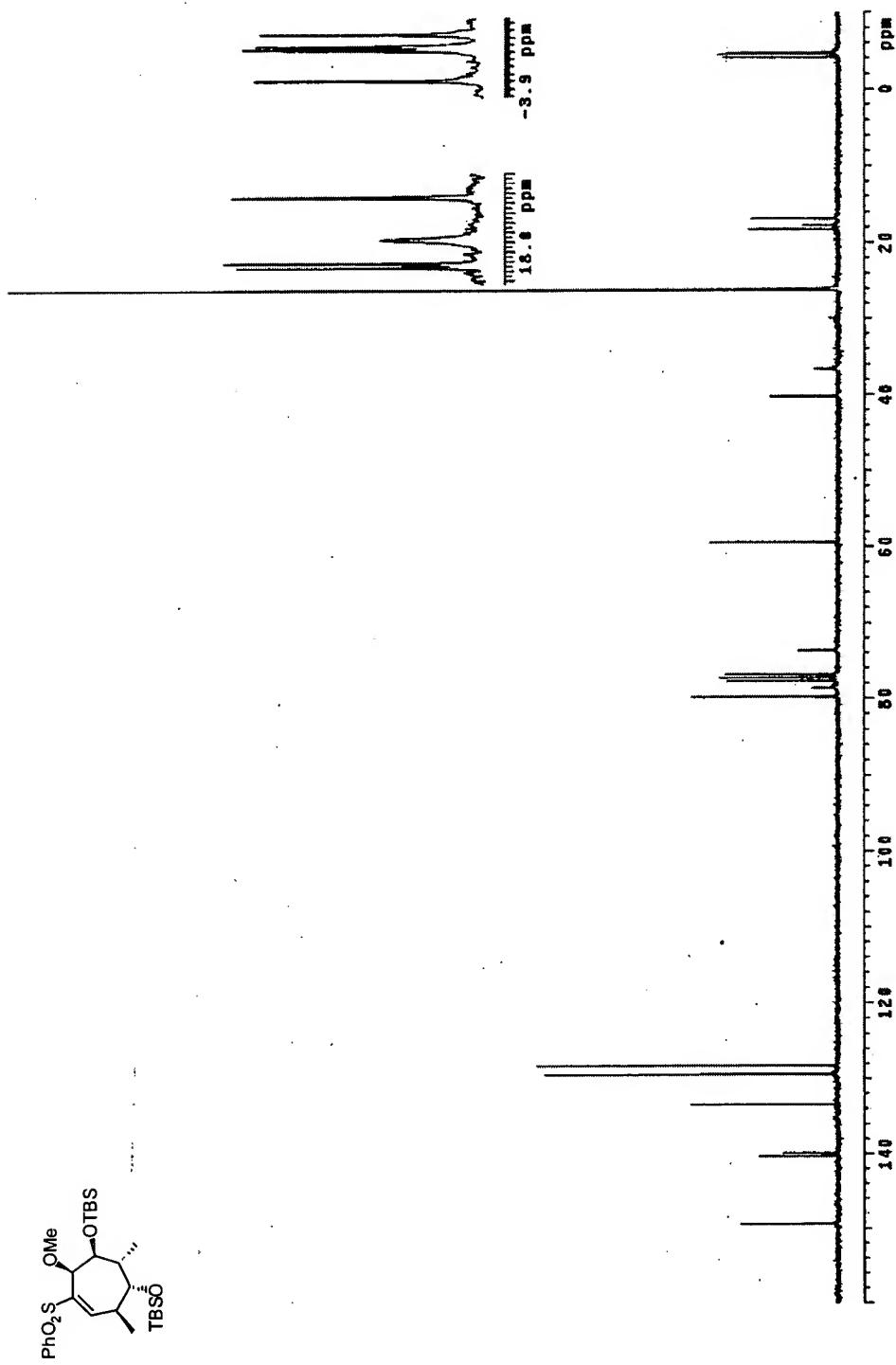
75MHz ^{13}C NMR of compound 52 in CDCl_3

FIGURE 8 (Cont'd)



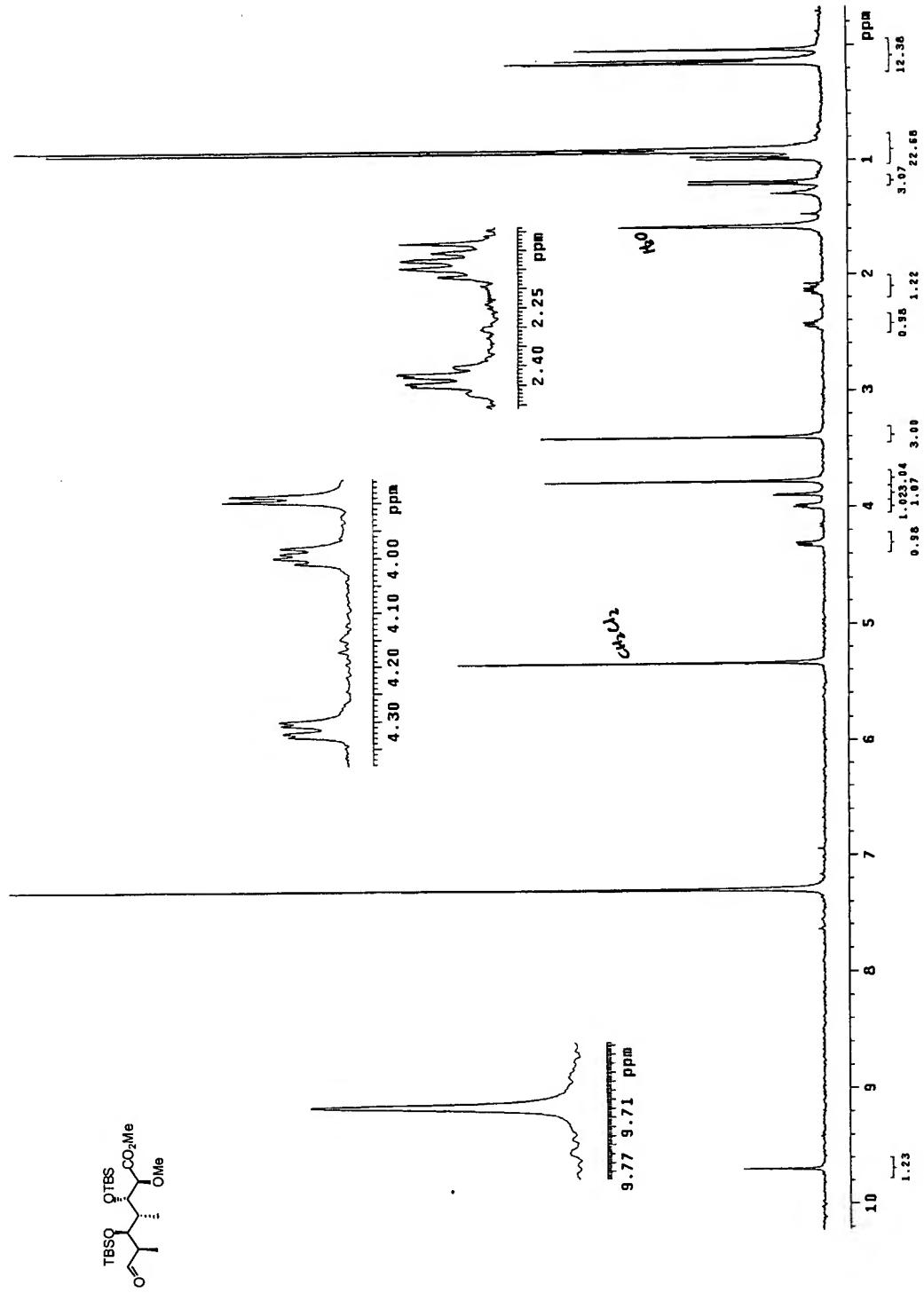
300MHz ^1H NMR of compound 53 in CDCl_3

FIGURE 8 (Cont'd)



75MHz ^{13}C NMR of compound 53 in CDCl_3

FIGURE 8 (Cont'd)



300MHz ^1H NMR of compound 51 in CDCl_3

FIGURE 8 (Cont'd)

